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Long-Term Trends in Water Quality for a High-Elevation Stream in the Great Smoky Mountains National Park: Impacts of Acid Deposition

Angela Vanessa Smith
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To the Graduate Council:

I am submitting herewith a thesis written by Angela Vanessa Smith entitled "Long-Term Trends in Water Quality for a High-Elevation Stream in the Great Smoky Mountains National Park: Impacts of Acid Deposition." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

John S. Schwartz, Major Professor

We have read this thesis and recommend its acceptance:

R. Bruce Robinson, Randall W. Gentry

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Long-Term Trends in Water Quality for a High-Elevation Stream in the Great Smoky Mountains National Park: Impacts of Acid Deposition

A Thesis
Presented for the
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Department of Civil and Environmental Engineering
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Angela Vanessa Smith
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Introduction

In the Southern Appalachians, high-elevation streams with small watershed areas tend to be sensitive to acid deposition (Deviney *et al.*, 2006; Cook *et al.*, 1994) because high elevations tend to have more cloud contact, leading to greater atmospheric deposition of pollutants containing sulfate and nitrate acids (Lovett and Kinsman 1990). In a recent study by Webb *et al.* (2004) examined the link between atmospheric acid deposition and stream water quality in brook trout (*Salvelinus Fontinalis*) streams in western Virginia and Shenandoah National Park (SNP). The study acknowledged that water quality improvement had been seen in response to reduced sulfate deposition in northern and eastern United States (U. S.) in regions that do not share the same watershed characteristics as the high-elevation Southern and Central Appalachians, which include SNP. In the study, Webb *et al.* concluded that soil characteristics were the factors that retained sulfate in the system and prevented proportional stream water quality improvement. This type of study is necessary to understand water quality reactions and anticipate the best conservation measures to implement.

Conservation of natural recourses for planetary health and benefits of future generations has been a concern in the U. S. since before the world's first national park was created. In 1782 conservation meant protection from settlers; in modern times it means protection from pollutants. As the culture changes and evolves, recourse management must also evolve. This sentiment was addressed in a memorandum from the office of Nancy Finley, Chief of Resource Management and Science for the GRSM, read "National Park managers are directed by federal law to know the status and trends in the

condition of natural resources under their stewardship in order to fulfill the National Park Service mission of conserving the scenery, and the natural and historic objects and wildlife in national parks unimpaired. In order to fulfill this mission, it is necessary to identify and understand changes in complex, variable and imperfectly understood natural systems and to provide insight into whether observed changes are within natural levels of variability or indicate excessive human influence."

The Noland Divide Watershed (NDW), centrally located in the Great Smoky Mountains National Park (GRSM), is both small and in a high elevation. NDW has been part of a long-term study on stream water quality and acid deposition since 1991 when it became part of the Inventory and Monitoring program of the GRSM. In an effort to identify and understand changes in the complex natural system at NDW several studies have been performed. The first study was the Integrated Forest Study, 1985-1991, which analyzed the impacts of atmospheric deposition on nutrient cycling in 13 research forests in the U. S. and Northern Europe, including NDW. This study, in order to accurately assess the atmospheric deposition, took measurements of air chemistry, hydrology, meteorological and canopy characteristics (Lindberg and Lovett, 1992). Another study compared ingress and egress of nitrogen fluxes through the nitrogen-saturated watershed (Van Miegroet *et al.*, 2001). Brewer *et al.* (2003) incorporated NDW into a nutrient modeling study, which predicted in the year 2040 with current reductions in nitrate and sulfate, stream water acid neutralizing capacity (ANC) would still not exceed 20 μeq/L. NDW was chosen for this study based on the low streamwater ANC, indicating that NDW is a sensitive or impaired surface water (Brewer *et al.,* 2003).

Sensitive streams are subject to episodic low pH events that can be toxic to aquatic life (Hall *et al.*, 1980). For some of the more stressed species, like the native brook trout which dwell in streams larger than those in the NDW, toxicity levels in the streams have occurred (Neff, 2007; Robinson *et al.*, 2006). Low pH interferes with the trout's normal body chemistry, for example the gill ion transport and influx and efflux of sodium (Booth *et al.*, 1988). In a recent study Neff found that during storm events, when pH values dropped to 4.66 instantaneously or to 5.0 for 20 hours, trout lost their ability to regulated critical sodium ions. Other species that are common food sources and key elements in the food web, like may flies (*Ephemeroptera*) and stone flies (*Plecoptera*), are reduced by degraded water quality (Hall *et al.*, 1980). Reduction of these three species is a clear indication that the GRSM has the need to manage the water quality of its streams in order to protect aquatic wildlife. Management of the water quality will require an understanding of the existing system with any long-term changes that are occurring and a concept of the fate and transport of acid deposition inside the watershed. This system trend analysis and relationship of deposition to stream water quality are the focus of this analysis.

The objectives of this study were to:

- Determine any long-term trends in the water chemistry for rainfall, throughfall, soil water, and streamwater for a high-elevation GRSM site impacted by acidic deposition.
- Infer and quantify any chemical drivers of stream acidification from atmospheric deposition of acid pollutants.

Background

Atmospheric Acid Deposition

Atmospheric acid deposition is sulfuric and nitric acids with ammonium transferred from air emission of sulfur dioxide, nitrogen oxides and ammonium (Driscoll *et al.*, 2002). Sources of these pollutants include fossil fuel combustion, industrial activities, mining, and metal processes (Hedin, 1996). Total acid deposition is the sum of wet, dry, and cloud deposition (Brewer *et al.*, 2003). See the following equation: Total Deposition = Precipitation + Dust + Cloud. Cloud and dust deposition in this document are simply referred to as dry deposition so as to differentiate it from deposition in precipitation. The following equation illustrates the definition of dry deposition for this document: Dry Deposition = Dust + Cloud.

Nitrate and Sulfate Deposition

Studies showed that high elevations in the GRSM, which would include the NDW, receive some of the highest loading rates of nitrogen and sulfur in North America (Johnson and Lindberg, 1992; Nodvin *et al.*, 1995). As a result of nitrate and sulfate concentrations, the average pH of precipitation in the United States is about 4.0 (Hall *et al.*, 1980) and in July of 1997 the U. S. Geological ,Society reports that the average pH of precipitation is between 4.2 and 4.4. In a nitrogen saturation study Stoddard (1994) concluded that the high rate of nitrogen deposition was degrading the surface water quality in the United States and that it was a cause of episodic acidification. He noted that for the area that includes NDW there may also be chronic acidification from nitrogen saturation. DeWalle and Swistock (1994) found that sulfate was the primary cause of ANC decline in streams in forested watersheds in the northern Appalachian Plateau of

Pennsylvania between October 1988 and April 1990.

Stream ANC

Acid neutralizing capacity (ANC) is used to determine a stream's degree of acidification and buffering capacity. Often ANC is used as the only indicator of stream water quality as it is a function pH and the resilience of the stream chemistry. The complete definition of ANC is the difference between the sum of proton acceptors and donors (Stumm and Morgan, 1981, Turner *et al.*, 1991). In most natural waters where carbonate is common, ANC can be defined by the following equation: $ANC = [HCO3^-] + 2[CO3^{2-}] + [HO^-] - [H^+]$ (Jensen 2003). For high elevation streams with typically low ANC values, like the NDW, ANC is often calculated by the following equation: $ANC = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] + [NH4^+] + [Al^{n+}] - [SO4^{2-}] - [NO3^-] - [Cl^-] - [F^-]$ (DeWalle and Swistock, 1994). One study of acid deposition in the Northeastern United States found that depressions in stream ANC occur during acidic episodes and periods of high stream flow and that values are usually at a maximum during summer base flow events (Driscoll *et al.*, 2001). Dennis *et al.*, (1995) in a Shenandoah National Park study found that streams in forested watersheds with thin, poor soils often have negative ANC values.

Stream pH

Episodic stream acidification was identified in the late 1980's as the most significant environmental problem from acid deposition (Lawrence, 2002). Sensitivity to acid deposition combined with greater exposure may allow episodic low stream pH reading, which have measured as low as 4.3 in the NDW (Shubzda *et al.*, 1995 and Robinson *et al.*, 2004). Low stream pH can be detrimental to aquatic life by increasing

concentrations of base cations, including aluminum (Hall *et al.*, 1980), which can be toxic to fish (Dennis *et al.*, 1995). In the Hubbard Brook experiment Hall *et al.*, (1980) discovered that stream acidification decreased diversity of species, increased the chances of a dominant species, and simplified the food web.

Stream Aluminum

Aluminum speciation in streamwater is a key function for aquatic life as several species, such as brook trout, have aluminum toxicity levels (Wood, 1990). The pH of streamwater controls aluminum speciation. The solubility of aluminum increases exponentially as pH falls below 5.6 with maximum toxicity to trout occurring at about pH 5 (Bulger *et al.*, 1998).

Conductivity

Conductivity is the measure of a solution's ability to conduct electricity. The conductance is the dissolved ions that carry the current through the solution. Dissolved solids are the main contributors to ionic strength (Snoeyink and Jenkins, 1980).

Modeling Water Quality

Stream water quality models have been developed based on different sorts of criteria or input variables. Because not every portion of natural systems can be recorded, the type of data collected is the key to modeling. Two common models and the types of data on which they are based are described below: one model, the Model of Acidification of Groundwater in Catchments (MAGIC), uses geology, soils, forest cover, and physical features to project stream water quality; another model, the Nutrient Cycling Model (NuMC), requires daily and monthly meteorological data and tracks hydrological and

chemical processes that control the exchange of nutrients between atmosphere, forest canopy, litter, soil, soil water, and streams (Brewer *et al.*, 2003).

NDW

The NDW is a high-elevation red spruce-Fraser fir forest in the Southern Appalachian Mountains. The watershed contains old-growth forests and poorly buffered soils and streams (Nodvin *et al.*, 1995). The forests have suffered declines in health from the exotic balsam woolly adelgid (Barker *et al.*, 2002). Dry and cloud deposition are major sources of nutrients such as nitrogen and sulfur for vegetation in the area (Lindberg and Lovett, 1992; Weathers *et al.*, 2006). The watershed receives high rates of nitrogen (about 1900 eq/hectare/year) and sulfur (about 2200 eq/hectare/year) in the form of atmospheric deposition (Nodvin *et al.*, 1995). Acidic atmospheric deposition has degraded the stream water quality in other areas to the degree that aquatic life suffered (Hall *et al.*, 1980).

Methods

Study Area

The NDW lies in high-elevation range of 1595 to 1940 meters (5,560 to 6,360 feet). The watershed covers an area of 17.4 hectares (43 acres). Figure 1 shows the GRSM with the NDW designated with a star. Figure 2 shows the watershed proportions.

Study Design

Five water quality monitoring sites were included in the study. The sites included two precipitation collecting sites, two stream monitoring sites, and a soil lysimeter site.

Wet precipitation only was collected at an open site (OS) platform equipped with a precipitation-triggered cover release. When rain water completed the circuit between two thin metal plates a motor would engage and move a weight which was attached to the ends of two rotating arms. At the other end of the two arms was the collector cover. When the motor was engaged the cover would be moved away from the collector. When

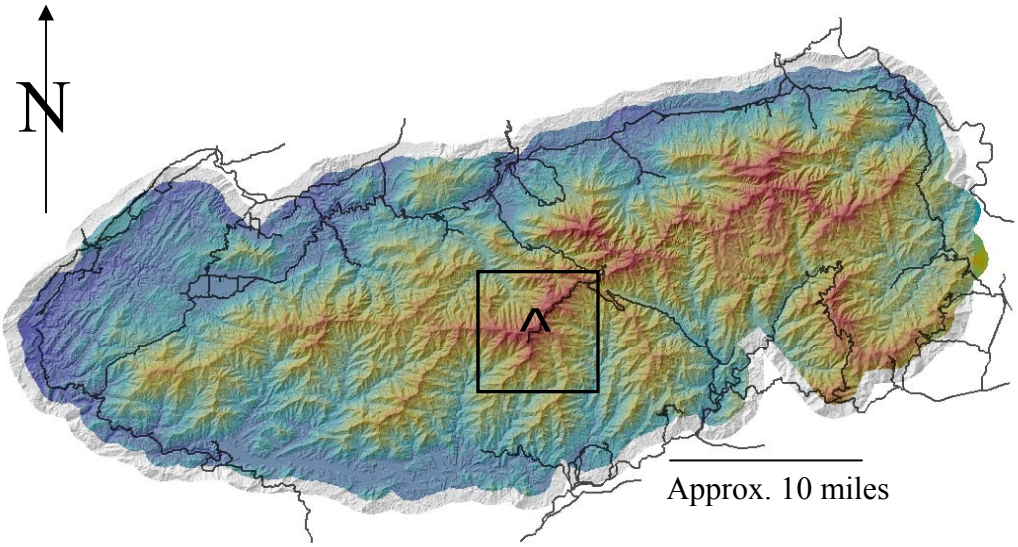

Figure 1: Great Smoky Mountains National Park with Elevation Detail and Noland Divide Watershed

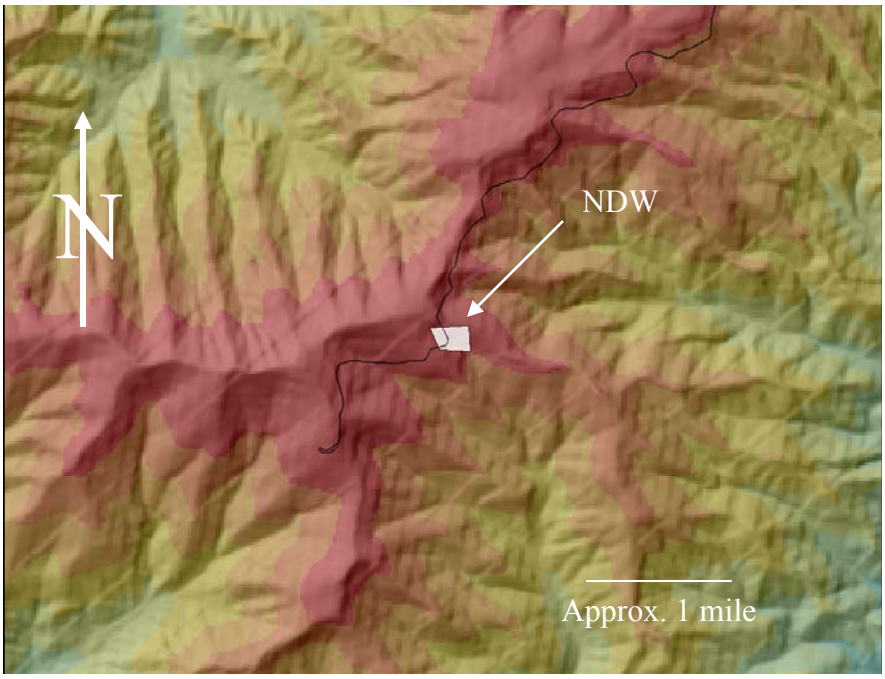

Figure 2: Detail of Noland Divide Watershed

collector. The collector consisted of a 10-inch funnel connected by 7 feet of black rubber tubing with hose clamps to a 10-gallon carboy. The carboy was placed inside a plastic housing which was buried ¾ of the way into the ground for insulation and protection. Figure 3, shows part of the OS collection system with the platform and collector cover.

Throughfall (TF) precipitation in July 1991 through December 2004 was collected by two 5-gallon bucket collectors with low density polyethylene (LDPE) liners. This system served in both summer and winter. Throughfall precipitation starting June 2004 was collected by 10 funnel collectors randomly disbursed under the spruce-fir forest canopy. Figure 4 shows a single TF collector. Eight-inch diameter funnels suspended approximately 1 meter above the forest floor were attached by hose clamps to ¾-inch black rubber tubing. The tubing fed vertically into LDPE 1-gallon brown jugs. The jugs

Figure 3: Photograph of the OS Collection System at Noland Divide Watershed

Figure 4: Photograph of a Single TF Collector

were housed in 5-gallon buckets and buried ¾ of the way into the ground for insulation and protection. The 10-collector system, known as summer protocol, was employed May through October and winter protocol, the two collector system, was employed November through April for years subsequent to the 2004 protocol change. Appendix A presented statistical comparison between the protocols showing that the observations were not shown to be different.

Two streamlets designated as southwest (SW) and northeast (NE) drain the watershed. Stream water samples were collected from these streams individually. Depth sensors placed in stilling wells inside H-flumes read the stream depths, which were then converted to a discharge. Both stream sites had continuous monitoring by YSI 600R sondes. The sondes were equipped with pH, conductivity, and temperature probes. The SW sonde was installed in July 1991 and the NE sonde was installed in April 1998. The two depth sensors and two sondes transmitted to a Campbell Scientific data logger which recorded data in 15-minute increments. The longer collection history of the SW streamlet was the only reason that the SW data was referenced primarily in this document over the NE. Appendix B includes analysis of the NE stream data and a correlation table, Table B-3, showing that most of the analytes of the two streamlets were correlated and all with p-values less that 0.000.

Chemistry Analysis

Samples were analyzed in the lab in accordance with manufacturer's instructions or Standard Methods. pH, conductivity, and ANC were analyzed with an auto-titrator. Anions and cations were analyzed by ion chromatography, atomic absorption spectrophotometry, or inductively coupled plasma spectrometry. Precipitation and soil

samples were not measured for ANC. All test methods for chemical analysis of water samples were followed using published protocols. Samples were analyzed at room temperature by procedures described in Table 1. Each analysis method had individually tailored QA/QC procedures in the form of spikes, splits, and replicates. An annual report is provided to the GRSM, which includes a balance of total anions and total cations per sample. Although organic acids are not included in the chemistry analysis, ions typically balance with less than a 5%. Samples that do not ion balance are re-analyzed. Organic acids most likely account for the percent error in the sample ion balances. Organic acids reduce ANC only slightly relative to sulfate and nitrate, which are the primary cause of reduced stream water ANC (DeWalle and Swistiock, 1994).

Statistical Analysis

Statistical analysis was performed for three functions: to prepare the database, to calculate basic descriptive statistic of the data, and to identify any trends. Unless stated otherwise SPSS 15.0 was used to calculate results. Commonly accepted methods were considered to prepare the database by eliminating outliers. Mahalonobis distances were used to determine outliers. In most cases Mahalonobis distances greater than 6 were eliminated from further analysis. Mean, median, standard deviation (Stdev), and coefficient of variance (CV) were calculated to provide a frame of reference and aid in any comparative study. Bivariate correlation analysis was used to determine if significant linear relationships exist between time and analyte concentrations as well as between different analytes. Significance was designated as a p-value of 0.01 or less (Montgomery and Runger, 2006). Correlation analysis was performed using Kendall's Tau.

Table 1: Procedure, Method and Equipment for Laboratory Analysis

Analyte	Procedure	Method	Equipment
pH	Potentiometric	EPA Method150.1	Man-Tech PC-Titration Plus
Conductivity		EPA Method 120.1	
ANC	Titration	Automated Gran Titration	
Ammonium	Ion Chromatography	Manufacturer's Instructions	Dionex
Chloride, Nitrate, and Sulfate	Ion Chromatography	Standard Methods 4110	Dionex
Aluminum, Copper, Iron, Manganese, Potassium, Silicon, Sodium, and Zinc	Inductively Coupled Plasma Spectrometry	EPA Method 6110B & 6110C	Thermal Elemental Iris Intrepid II
Calcium and Magnesium (October 1998 through May 2003)	Atomic Absorption	Standard Methods 3111	Instrumentation Laboratory
Calcium and Magnesium (June 2003 through 2007)	Inductively Coupled Plasma Spectrometry	EPA Method 6110B & 6110C	Thermal Elemental Iris Intrepid II

Key water quality parameters ANC, pH, conductivity, chloride, nitrate, and sulfate were modeled using the stepwise multiple linear regression. These parameters were chosen to model because they are commonly regarded indicators of water quality for high-elevation and acid sensitive streams (Johnson and Lindberg, 1992; Cook *et al*., 1994). For independent variables, primary variables were used in the first step of the modeling process and then appropriate transforms of the primary variables. Primary variables are the system input variables from precipitation, deposition and time. Precipitation data was obtained from the National Climatic Data Center website. The flux variables are calculated from measured values. Flux variables, given in equivalents per hectare per year, normalize the concentration to the amount of precipitation. Essentially the flux variables relate the amount of an analyte, rather than concentration, to a unit area over a time period. Table 2 shows the primary variables for this system with descriptions and ranges relevant to the data sets in this study. The minimum concentrations for many of the parameters were below the detection limits (BDL) of the analysis methods. The variables were set to enter the model if the probability of the partial F statistic was less than or equal to 0.05 and set to leave if the partial F statistic was greater than or equal to 0.10. These criteria were used for all models. To insure statistical significance, only models with a p-value less than or equal to 0.05 were considered. The independent variables in the model also had to be statistically significant at a p-value of 0.10 or less. A variance inflation factor (VIF) over 10 and informal multicollinearity diagnostics such as Spearman and Pearson bivariate were used

Table 2: Primary Variables with Description and Range

Primary Variable	Description	Range
Date	Julian date	33417-39085
Year_Day	Day of the year	1-365; 1-366 on leap years
Dry_Days	Number of days without significant precipitation prior to and including sampling day	0-16
Dry_Chem	Number of days of accumulation of dry deposition prior to last precipitation event plus the number of days over which the sample was collected	0-37
SW_Q	Flow in cfs for SW stream	0.01-2.78
OS_pH	pH at OS	3.68-6.21
OS_Cond	Conductivity in μS/cm² at OS	2.1-64.3
OS_Vol	Volume in cm collected at OS	0.0-27.6
OS_Cl	Chlorine concentration in μeq/L at OS	BDL-319.8
OS_NO3	Nitrate concentration in μeq/L at OS	BDL-64.9
OS_SO4	Sulfate concentration in μeq/L at OS	BDL -140.6
OS_Na	Sodium concentration in μeq/L at OS	BDL -219.6
OS_NH4	Ammonium concentration in μeq/L at OS	BDL -77.3
OS_K	Potassium concentration in μeq/L at OS	BDL -834.9
OS_H	Hydrogen ion concentration in μeq/L at OS	BDL -5201.2

Table 2: Cont.

Primary Variable	Description	Range
OS_N	Inorganic nitrogen concentration in μeq/L at OS	BDL -131.7
OS_Cl_ Flux	Chloride flux in eq/hectare/year at OS	BDL -8021
OS_NO3_Flux	Nitrate flux in eq/hectare/year at OS	BDL -2718.3
OS_SO4_ Flux	Sulfate flux in eq/hectare/year at OS	BDL -3171
OS_NH4_ Flux	Ammonium flux in eq/hectare/year at OS	BDL -1686
OS_H_Flux	Hydrogen ion flux in eq/hectare/year at OS	BDL -3469
OS_Mg	Magnesium concentration in μeq/L at OS	BDL -87.2
OS_Ca	Calcium concentration in μeq/L at OS	BDL -185.9
TF_pH	pH at TF	3.48-5.39
TF_Cond	Conductivity in mS/cm² at TF	8.2-230.0
TF_Vol	Volume in cm collected at TF	0.2-34.3
TF_Cl	Chlorine concentration in μeq/L at TF	BDL -396.2
TF_NO3	Nitrate concentration in μeq/L at TF	BDL -401.1
TF_SO4	Sulfate concentration in μeq/L at TF	BDL -594.7
TF_Na	Sodium concentration in μeq/L at TF	BDL -373.3
TF_NH4	Ammonium concentration in μeq/L at TF	BDL -160.7

Table 2: Cont.

Primary Variable	Description	Range
TF_K	Potassium concentration in μeq/L at TF	BDL -731.2
TF_H	Hydrogen ion concentration in μeq/L at TF	4.1-331.1
TF_N	Inorganic nitrogen concentration in μeq/L at TF	BDL -510.9
TF_Cl_ Flux	Chloride flux in eq/hectare/year at TF	BDL -7511
TF_NO3_Flux	Nitrate flux in eq/hectare/year at TF	BDL -5646
TF_SO4_ Flux	Sulfate flux in eq/hectare/year at TF	BDL -8284
TF_NH4_Flux	Ammonium flux in eq/hectare/year at TF	BDL -3127
TF_H_ Flux	Hydrogen ion flux in eq/hectare/year at TF	BDL -5945
TF_Mg	Magnesium concentration in μeq/L at TF	BDL -567.9
TF_Ca	Calcium concentration in μeq/L at TF	BDL -1370

to identify multicollinearity. VIF greater than 10 may indicate excessive influence on the least squares estimates (Helsel and Hirsch, 1992, Neter *et al*., 1996). In stepwise regression independent variables were systematically removed to generate a model with the highest adjusted R-square value and minimal multicollinearity. Higher R-square values indicate that the model accounts for more of the variability in the data (Tamhane, 2000). Partial regression plots were used to identify influential data which are indications of nonlinearity (Fox, 1997). An influential data point is one that has high leverage and is a large outlier (Helsel and Hirsch, 1992). In the occurrence of a high Cook's D and that the data point was an outlier the point was considered for removal from the set. The data point was only removed if it could be well justified and was chemically inconsistent with other observations from the same collection day. 12 data points were removed based on these criteria. Approximately 1% of the data had partially missing information and was eliminated from the regression analysis.

The principle of parsimony was applied for choosing among models. This principle assumes that if all else is equal a simpler model is better (DeLurgio 1998). Curvature and heteroscedasticity of the residuals, indicating a non-random error distribution, were checked by plotting standardized residuals versus predicted values. Normality of the residuals was checked by observation of the normal probability plot. Partial regression plots were also observed to ensure linear relationships exist between the independent variables and the dependent variables when the other independent variables had been taken out. Transformation of the dependent variable can be used to linearize the partial regression plots (Neter *et al.*, 1996). The reasonableness of predicted constituent coefficients was also evaluated. Therefore, the simplest model that explains a

comparable amount of the variability and adheres to the assumptions of regression was chosen as the best model.

Natural settings can be challenging when researchers and equipment are unable to accommodate harsh environments. Water temperatures can range from zero to twenty degrees Celsius. High intensity precipitation events result in stream flows that carry great energy and force. Animal curiosity often resulted in damaged or disconnected equipment. These combined effects sometimes resulted in some lost data and damaged equipment. This watershed was subject harsh environmental factors that could have entered large amounts variation into the data set, which although true and correct readings, may appear as extreme outliers and have been very difficult to account for in a model and resulting in lower R-squared values. Another source of error could have been in not tracking organic acid concentrations.

Results and Discussion

Chemistry Analysis

Descriptive statistics were presented to provide comparisons between the collection sites. The precipitation sites, OS and TF, were the primary system locations of influx and the SW was the primary location efflux. Comparing mean concentrations gave an idea of the fate and transport of several water quality parameters. Table 3 summarized the descriptive statistics including mean, median, standard deviation (stdev), and coefficient of variance (CV) for SW, OS, and TF for the following parameters: ANC, precipitation, pH, chloride, nitrate, sulfate, ammonium, sodium, potassium, magnesium, calcium, hydrogen, aluminum, copper, iron, manganese, silicon, and zinc. For most of the parameters presented in Table 3, TF showed a higher mean concentration than OS. Dry acid deposition was most likely the reason for these differences (Weathers *et al.*, 2006).

ANC

TF exhibited the lowest mean ANC value of the three collection sites. Dry deposition of nitric and sulfuric acid is most likely the cause for the lower value than OS. Both OS and TF had lower ANC values than SW most likely because the stream water comes in contact with the soil and other possible ANC contributors. The mean ANC for SW of 12.06 μeq/L is low relative to most surface waters, but typical of streams exhibiting degradation and with this elevation and watershed characteristics (Eshleman and Kaufmann, 1988; Brewer *et al*., 2003; Sullivan *et al.*, 2007).

Table 3: SW, OS, and TF Water Quality Parameter Mean, Median, Standard Deviation, and Coefficient of Variance

Site	Statistic	ANC, μeq/L	Precipitation collected per sample, cm	pH	Conductivity, μS/cm2	Cl, μeq/L	NO3, μeq/L	SO4, μeq/L	NH4-N, μeq/L	Na, μeq/L
SW	Mean	12.06	--	5.81	12.54	15.72	38.97	28.71	0.61	26.80
	Median	11.17	--	5.83	12.49	13.42	38.65	28.37	BDL	25.37
	Stdev.	9.27	--	0.29	1.51	8.24	6.72	5.08	2.74	7.64
	CV	76.90	--	4.98	12.08	52.39	17.24	17.70	445.99	28.52
OS	Mean	-4.78 *	7.70	4.73	13.93	10.28	16.07	34.08	19.46	6.79
	Median	-2.39 *	7.05	4.67	12.05	7.10	13.06	28.00	15.50	5.18
	Stdev.	21.00 *	5.27	0.43	8.41	19.51	11.81	23.25	20.27	6.61
	CV	-438.91 *	68.47	9.18	60.35	189.80	73.50	68.22	104.17	97.48
TF	Mean	-6.76 *	8.38	4.28	44.98	32.05	50.58	104.34	25.97	30.73
	Median	0.00 *	7.13	4.22	37.85	24.52	38.56	86.94	17.66	19.81
	Stdev.	13.56 *	6.31	0.37	27.20	29.71	50.14	72.79	26.64	38.98
	CV	-200.67 *	75.32	8.56	60.47	92.71	99.13	69.76	102.57	126.87

*OS and TF ANC descriptive statistics are based on a two-year history.
-- Stream water, not precipitation, was collected at this site.

Table 3: Cont.

Site	Statistic	K, μeq/L	Mg, μeq/L	Ca, μeq/L	H, μeq/L	Al, ppm	Cu, ppm	Fe, ppm	Mn, ppm	Si, ppm	Zn, ppm
SW	Mean	8.09	18.26	47.83	6.74	0.04	0.01	0.01	BDL	1.74	0.02
	Median	7.07	18.64	47.38	1.66	0.03	BDL	0.01	BDL	1.79	0.01
	Stdev.	4.20	3.37	4.58	12.74	0.04	0.01	0.01	0.01	0.29	0.03
	CV	51.85	18.43	9.58	188.96	98.31	166.03	137.34	177.81	16.77	171.01
OS	Mean	8.71	2.92	12.51	27.69	0.04	0.01	0.01	0.01	0.06	0.09
	Median	3.10	1.89	9.20	21.38	0.02	BDL	BDL	BDL	0.03	0.04
	Stdev.	23.62	3.37	11.65	24.49	0.09	0.03	0.03	0.01	0.22	0.11
	CV	271.19	115.39	93.13	88.43	236.33	255.29	224.82	114.66	353.72	128.19
TF	Mean	47.58	21.58	58.57	65.84	0.09	0.01	0.03	0.12	0.12	0.15
	Median	30.60	15.19	43.96	56.27	0.08	BDL	0.03	0.10	0.11	0.08
	Stdev.	52.31	20.00	47.34	54.84	0.06	0.02	0.03	0.10	0.08	0.22
	CV	109.96	92.68	80.83	83.29	67.00	211.26	82.96	83.34	67.67	150.55

Precipitation

Mean amounts of precipitation showed that OS collections averaged 7.70 cm and TF collections averaged 8.38 cm between sampling days. The amount of precipitation collected at OS is understandably less than at TF as a function of the collection device. Since the OS required a threshold amount of water to make the connection between the switch plates, mist and heavy dew that could condense on the TF funnels may have escaped the OS collector.

pH and Hydrogen

TF showed the lowest mean pH value of the other collection sites at 4.28. OS and SW showed mean pH values of 4.73 and 5.81 respectively. This was most likely due to dry acid deposition; witch was collected with the water samples at TF. This is supported by a 1992 National Atmospheric Deposition Program report to Congress where it was stated that cloud water pH at a neighboring monitoring site (CLD303) ranged between 3.2 and 3.9.

Chloride

The mean chloride value was highest at TF (32.05μeq/L). This was most likely due to dry deposition. The mean SW chloride value of 15.72μeq/L was between the TF and OS (10.28μeq/L). These relative concentrations are indicative of a chloride saturated system, where dry deposition is the primary inlet and precipitations acts to wash the excess off of the vegetation and out of the soil into the stream. This pattern is echoed in the relative concentrations of some of the other analytes that are indicators of water quality and addresses their fate and transport.

Nitrate

The mean nitrate concentration for TF (50.58 μeq/L) was higher than OS and SW, 16.07 μeq/L and 38.97 μeq/L respectively. Stream water nitrate appeared to have followed the same trend as chloride. Plant uptake also could explain the difference in concentrations; however NDW had experienced a net degeneration of vegetation over the course of this study (Weathers, 2006; Brewer, 2003). Other studies have also found that the NDW was nitrogen-saturated (Nodvin *et al*, 1995; Barker *et al*, 2002).

Sulfate

The mean sulfate concentration at TF (104.34 μeq/L) was greater than OS and SW, 34.08 μeq/L and 28.71 μeq/L respectively. Since acid deposition primarily consists of sulfuric and nitric acids, it explained why the mean sulfate concentrations at the three collection sites had the same pattern as pH with the stream sulfate concentration being less than the two precipitation sites. Plant uptake most likely contributes to the difference in concentrations.

Ammonium

The mean ammonium concentrations for TF and OS, 25.97μeq/L and 19.46μeq/L respectively, were greater than SW (0.61 μeq/L). It was assumed that the ammonium was reacting in the system because a relatively low concentration was leaving the system. Plant uptake and microbial activity would decrease the outgoing ammonium.

Sodium

The mean sodium concentrations for the three collection sites followed the same pattern as chloride and nitrate with the TF having been the largest and the OS having been the smallest of the three.

Potassium

The mean potassium concentration for TF (47.58 μeq/L) was higher than OS and SW, 8.71 μeq/L and 8.09 μeq/L respectively. This pattern is consistent with chloride, nitrate, and sodium.

Magnesium and Calcium

Mean calcium concentrations were more than twice that of magnesium for all three collection sites. The mean concentrations of magnesium and calcium followed the same pattern as chloride, nitrate, sodium, and potassium.

Aluminum

The mean aluminum concentration for TF (0.09 μeq/L) was larger than for OS and SW (0.04 μeq/L for both). The mean aluminum concentrations followed the same pattern as the mean pH values most likely because aluminum speciation is pH sensitive in these pH ranges (Snoeyink and Jenkins, 1980).

Copper and Iron

Concentrations of copper and iron were too low to report in units of μeq/L and were, therefore, reported in parts per million (ppm). The mean concentrations for all three collection sites were 0.01 ppm except iron at TF, which is 0.03 ppm.

Silicon

Concentrations of silicon were too low to report in units of μeq/L and were, therefore, reported in ppm. The mean silicon concentration for SW (1.74 ppm) is greater than for TF and OS, 0.12 ppm and 0.06 ppm respectively. This was assumed to be a function of contact with soil.

Manganese and Zinc

Concentrations of manganese and zinc were too low to report in units of μeq/L and were, therefore, were reported in ppm. The mean manganese and zinc concentrations were similar at each collection site. TF showed concentrations of 0.12 ppm for manganese and 0.15 ppm for zinc. The SW concentrations were also close at below detection limits (BDL) and 0.02 ppm for manganese and zinc respectively. The difference occurs at OS where the mean zinc concentration was 0.09 ppm and manganese was lower at 0.01 ppm. This difference indicated that a larger amount of zinc than manganese was entering the system as dry deposition.

Statistical Analysis: Temporal

Bivariate correlations with time were presented in two ways. The first correlations were linear time trends using Julian date. These correlations revealed long-term trends in water quality. The second correlations were for seasonality, which used day of year to reveal annual cycles and seasonal trends.

Linear time trends were presented for SW, OS, and TF for the following parameters: ANC, pH, conductivity, chloride, nitrate, sulfate, ammonium, and aluminum. Table 4 showed the mean, slope, R-square, and p-value for each correlation.

ANC

The SW ANC was decreasing at a rate of 0.054μeq/L/yr. Decreasing ANC is a commonly noted sign of stream water quality degradation (Brewer *et al.*, 2003; De Walle and Swistock, 1994). pH is a contributor of ANC and this trend of degrading water quality was seen in the pH results as well.

Table 4: SW, OS, and TF Water Quality Parameter Mean, Time Trend, R-square, and P-value (1991-2006)

Site	Description	ANC, μeq/L	pH	Conductivity, μS/cm²	Cl, μeq/L	NO3, μeq/L	SO4, μeq/L	NH4-N, μeq/L	Al, ppm
SW	mean	12.06	5.81	12.54	15.72	38.97	28.71	0.61	0.04
	time trend slope per year	-0.054	-0.005	-0.052	0.286	-0.668	-0.052	-0.005	-0.002
	time trend R-square	0.001	0.008	0.008	0.013	0.173	0.002	0.000	0.023
	time trend p-value	0.452	0.029	0.029	0.005	0.000	0.317	0.826	0.174
OS	mean	--	4.73	13.93	10.28	16.07	34.08	19.46	0.04
	time trend slope per year	--	0.011	-0.209	0.320	0.001	-0.160	0.460	-0.002
	time trend R-square	--	0.014	0.007	0.004	0.010	0.001	0.023	0.059
	time trend p-value	--	0.010	0.064	0.181	0.029	0.532	0.001	0.038
TF	mean	--	4.28	44.98	32.05	50.58	104.34	25.97	0.09
	time trend slope per year	--	0.016	-1.305	0.375	-0.204	-3.041	1.197	0.000
	time trend R-square	--	0.045	0.025	0.002	0.000	0.020	1.197	0.000
	time trend p-value	--	<0.000	<0.000	0.354	0.757	0.002	<0.000	0.926

-- ANC was not recorded for these collection sites for an adequate history.

pH

SW pH was decreasing with time at a rate of 0.005 pH units per year, whereas OS and TF were increasing with time, 0.011 and 0.016 pH units per year respectively. pH trends were consistent with other studies (Brewer *et al.,* 2003; Lawrence, 2001) . Brewer *et al.,* (2003) showed that depositional pH increased with time; while stream water pH, in that study, continued to be relatively constant. The results were supported by other studies that showed sulfate and nitrate deposition had decreased since the enactment of recent air quality legislation (U. S. Environmental Protection Agency, 2000; Burns *et al.,* 2006; Webb *et al.,* 2004). The most likely cause for the decreased stream water pH was identified by Lawrence (2001) who wrote that accumulation of nitrogen and sulfur in the forest soil from decades of acid deposition will delay stream recovery from episodic pH lows.

Conductivity

Conductivity was decreasing at all three collection sites. The decreases were at rates of 0.052 μeq/L/ yr, 0.209μeq/L/ yr, and 1.305 μeq/L/ yr for SW, OS, and TF respectively. By definition, this indicates that progressively fewer total ions were being deposited.

Chloride

Chloride deposition was increasing at all three collection sites at rates of 0.375 μeq/L/ yr, 0.320 μeq/L/ yr, and 0.286μeq/L/ yr for TF, OS, and SW respectively. Since both OS and TF chloride concentrations were increasing at a similar rate it was assumed that dry deposition was not the vehicle. Rather, chloride must have been dissolved in precipitation drops.

Nitrate

Nitrate showed no trend at TF with a p-value of 0.757. SW was decreasing at rates of 0.0.668 μeq/L/ yr, while OS was relatively constant at 0.001μeq/L/ yr. This was most likely because OS did not allow contact with plants and soil prior to collection like TF and SW. The nitrate decreasing in the stream was most likely a function of the vegetation (leaves in the canopy and roots along the stream) using the nitrate for metabolic processes (Nodvin *et al.*, 1995) and further may indicates forest regrowth.

Sulfate

Sulfate was decreasing at TF at a rate of 3.041 μeq/L/yr. OS and SW showed no trend with p-values of 0.532 and 0.317 respectively. Reduction in sulfate deposition was consistent with a recent study of the western Virginia and Shenandoah National Park. Webb *et al.,* (2004) found that sulfate deposition declined 40% from 1985 to 2000. From 1992 to 2000 NDW has seen a reduction in average annual sulfate flux at the TF site of 67%. A U.S. Environmental Protection Agency progress report (2000) correlated sulfate deposition decreases to the implementation of Title IV of the Clean Air Act Amendments of 1990, which has reduced sulfate emissions from power plants.

Ammonium

Ammonium showed no tend at TF with a p-value of 0.826. OS was increasing at a rate of 0.460 μeq/L/ yr. Ammonium contributes to acid deposition, but considerably less than nitrate and sulfate (Driscoll *et al.*, 2003).

Aluminum

Aluminum trends were relatively consistent at all three collection sites. OS and SW showed that aluminum deposition was slightly decreasing at both sits at a rate of 0.002 μeq/L/ yr. The TF aluminum showed no trend with a p-value of 0.926.

Data for key analytes along with long-term trends from Table 4 were plotted. The OS data were presented in the next three figures. Figure 5 showed pH, sulfate, and inorganic nitrogen plotted with pH in order to show the relationship of the trends. pH and inorganic nitrogen were increasing at a similar rate as both y-axes have logarithmic scales. Figure 6 showed calcium and magnesium data plotted with trends. The figure showed that calcium increased at rate larger than magnesium. Similarly nitrate

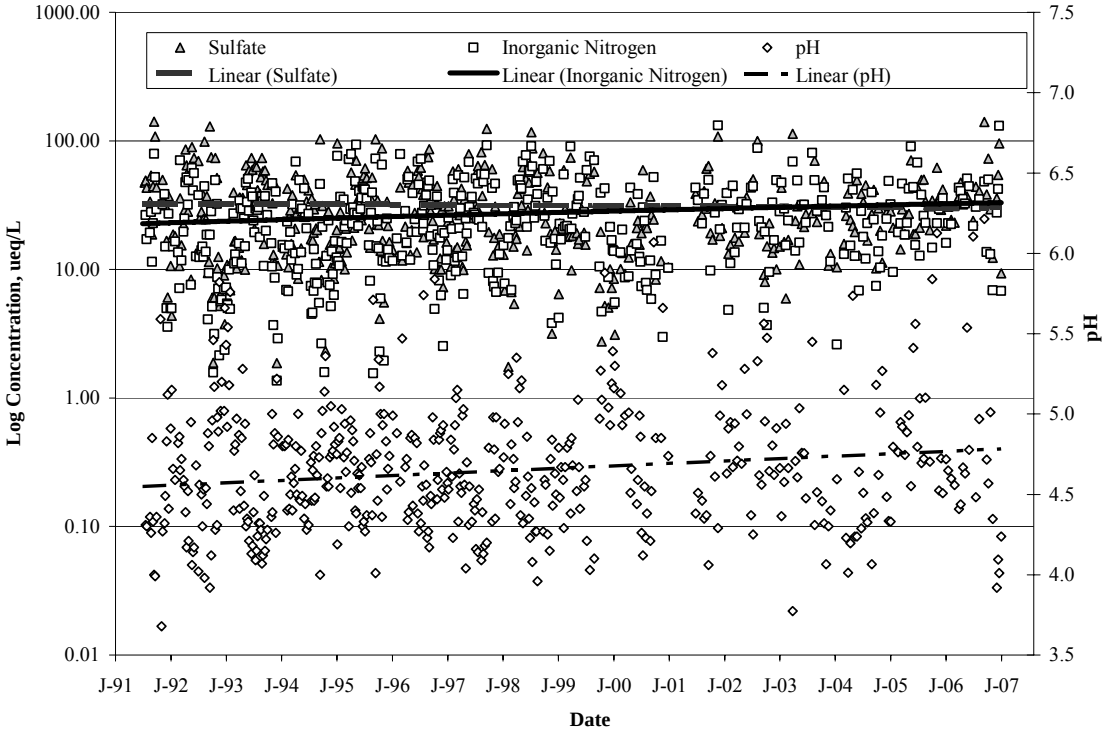

Figure 5: Time Trends of pH, Sulfate, and Inorganic Nitrogen with pH for OS

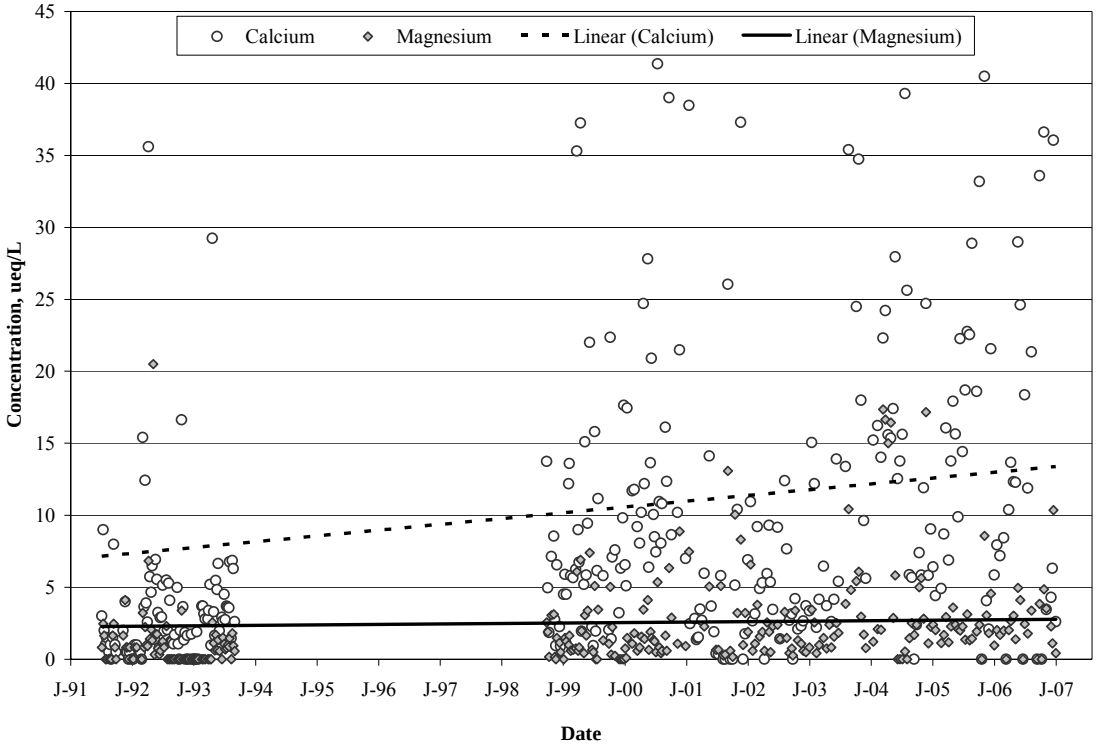

Figure 6: Time Trends of Calcium and Magnesium for OS

and ammonium were plotted together in Figure 7. Ammonium increased at a rate larger than nitrate.The data and time trends for throughfall were plotted in Figures 8, 9, and 10. Figure 8 showed pH, sulfate, and inorganic nitrogen plotted with pH in order to show the relationship of the trends. Like OS, pH and inorganic nitrogen were increasing with time and sulfate was decreasing. Figure 9 showed calcium and magnesium data plotted with trends. The figure showed that calcium and magnesium were relatively constant. Similarly nitrate and ammonium were plotted together in Figure 10. Unlike at OS, TF ammonium increased at a rate larger than nitrate.

Comparison of OS and TF deposition was represented in bar charts of key

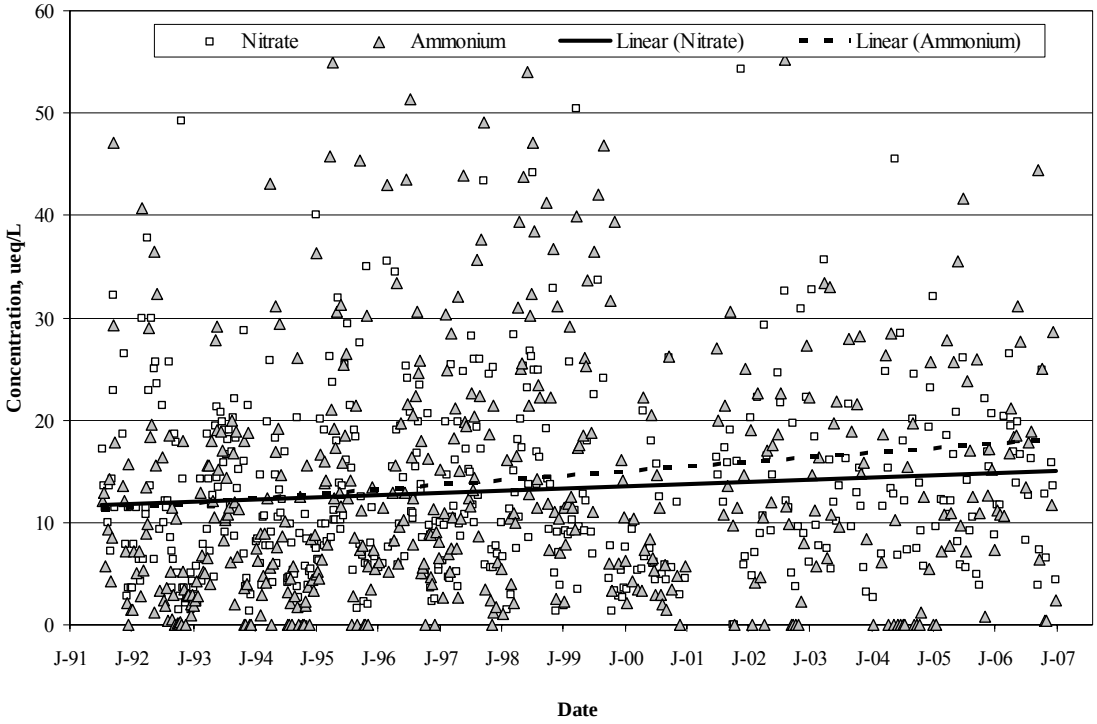

Figure 7: Time Trends of Nitrate and Ammonium for OS

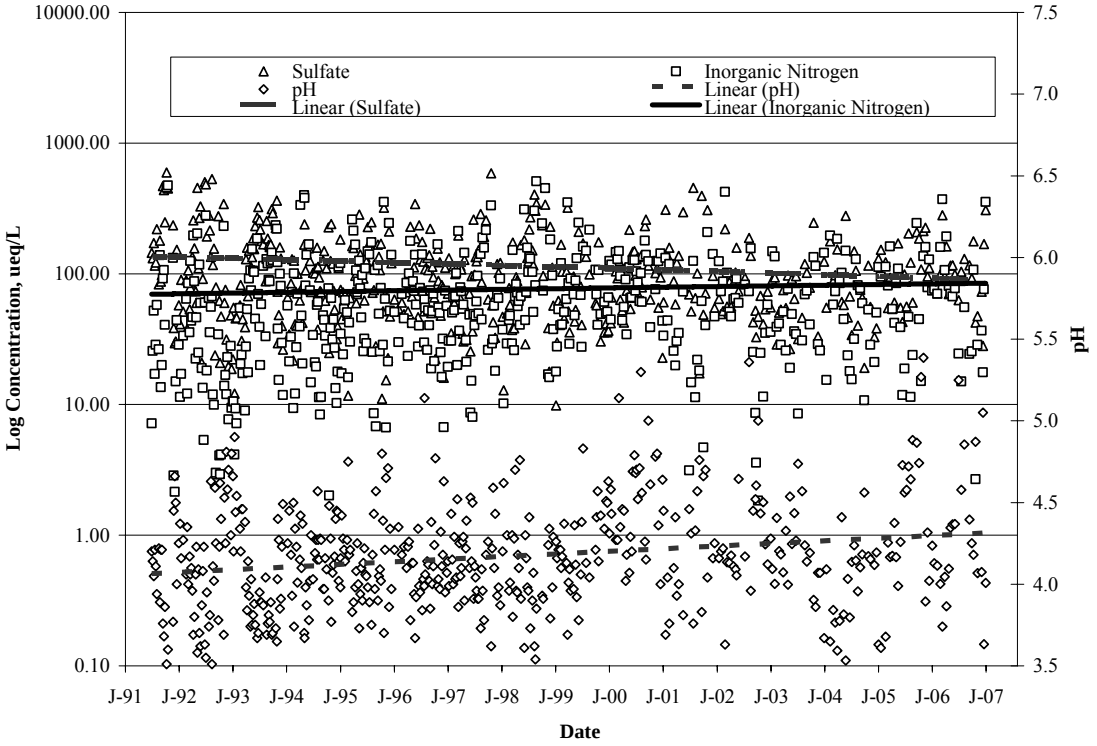

Figure 8: Time Trends of sulfate and inorganic nitrogen with pH for TF

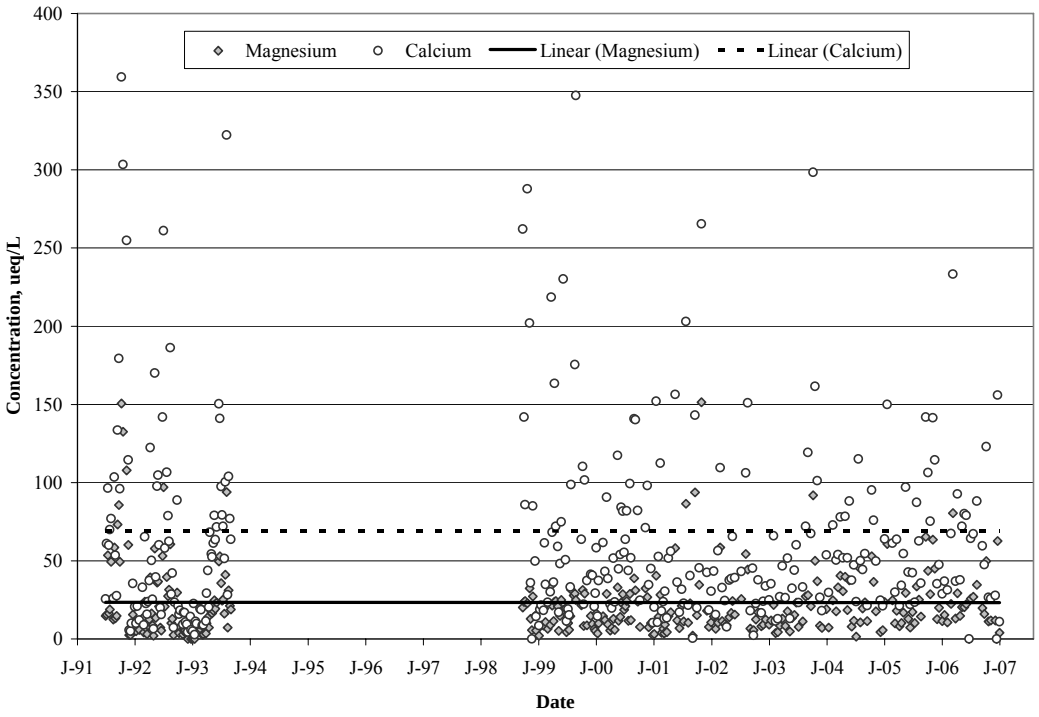

Figure 9: Time Trends of Calcium and Magnesium for TF

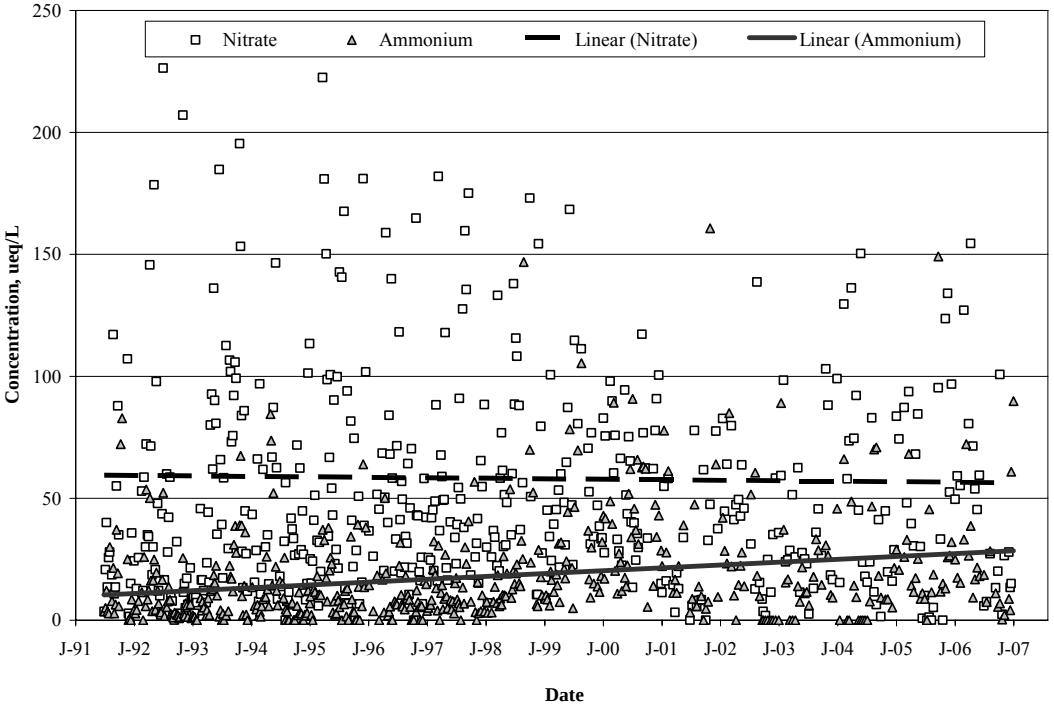

Figure 10: Time Trends of Nitrate and Ammonium for TF

parameters. The deposition was given in flux calculated by, first, normalizing the concentration of the individual samples to the amount of precipitation collected, next, multiplying by the ratio of the area of the watershed to the area of the collector, and last, converting the concentration to equivalents. These values were summed for each year. Figure 11 gave side-by-side comparison of calcium and magnesium for OS and TF. The difference in deposition of TF over OS was most likely due to dry deposition. This was true for Figures 12 and 13 as well. Depositional fluxes for OS and TF were presented to graphically display the rate of deposition in equivalent charge over a unit area over a time period. Depositional flux was anticipated to be proportional to the amount of precipitation. Figure 14 showed depositional fluxes for nitrate, sulfate, and ammonium with precipitation for OS. In most cases the deposition was consistent with the amount of precipitation. The exception was sulfate in 2001 where an unproportionately large deposition occurs. The TF fluxes in Figure 15 were consistent with precipitation as

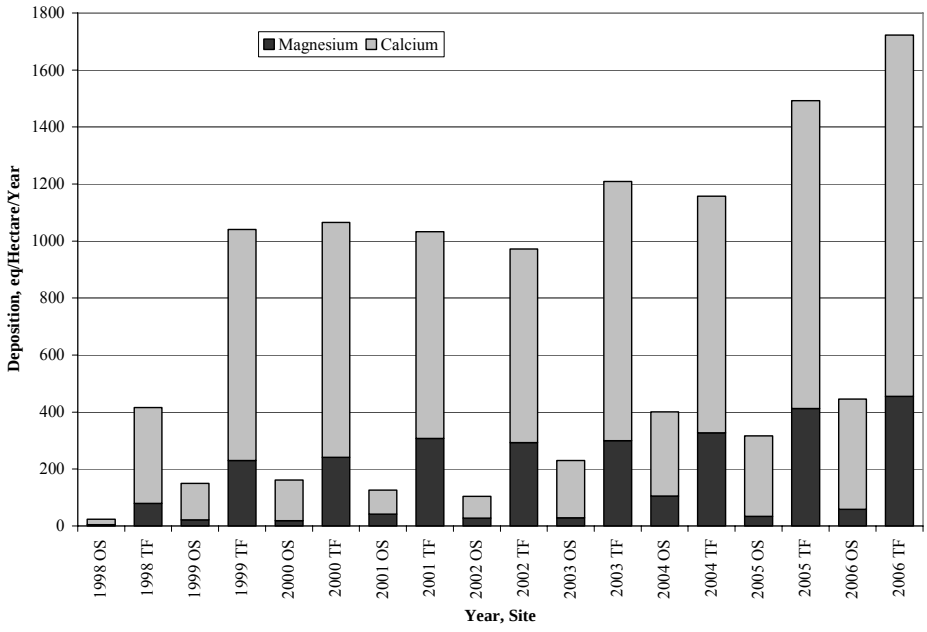

Figure 11: Deposition of Magnesium and Calcium for OS and TF

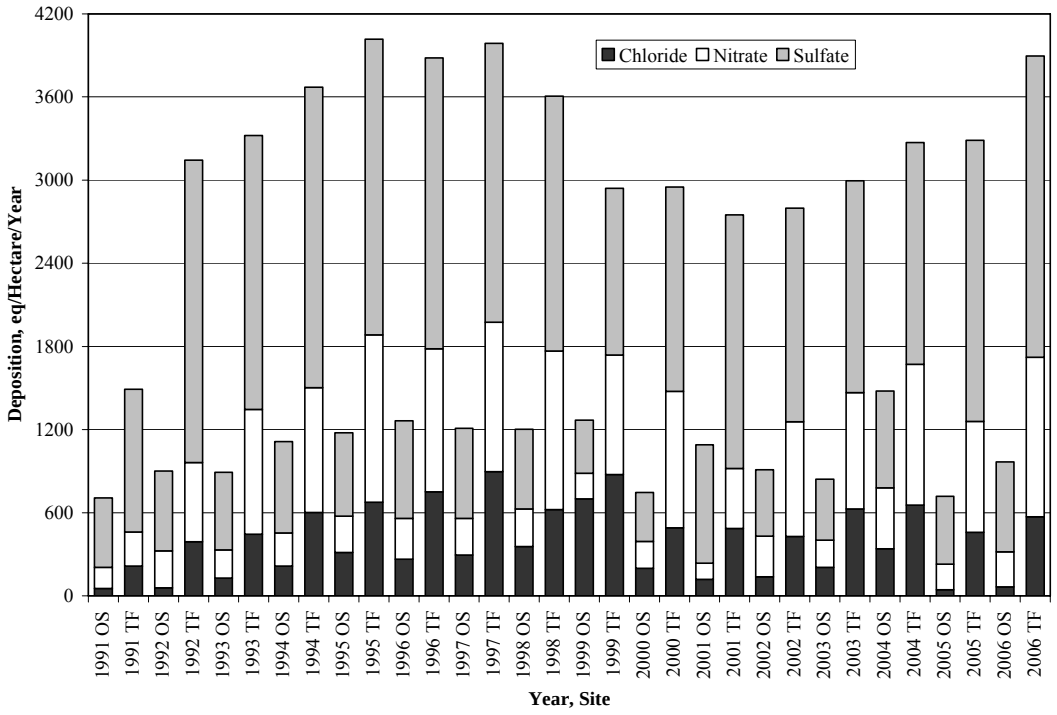

Figure 12: Deposition of Chloride, Nitrate, and Sulfate for OS and TF

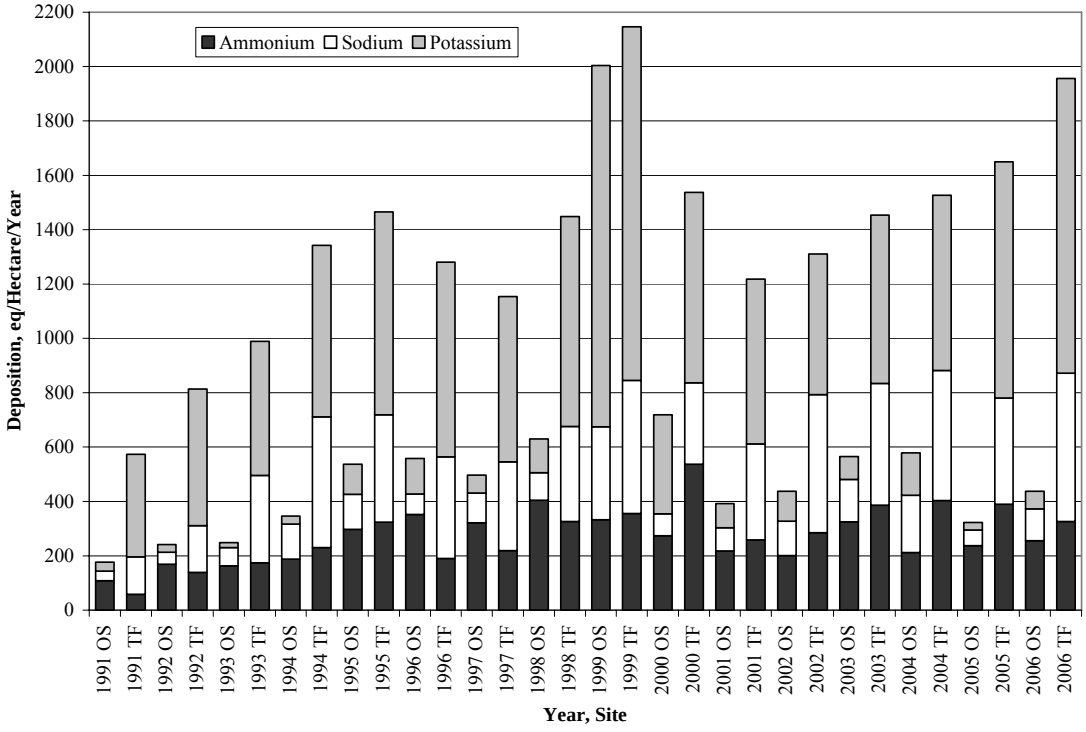

Figure 13: Deposition of Ammonium, Sodium, and Potassium for OS and TF

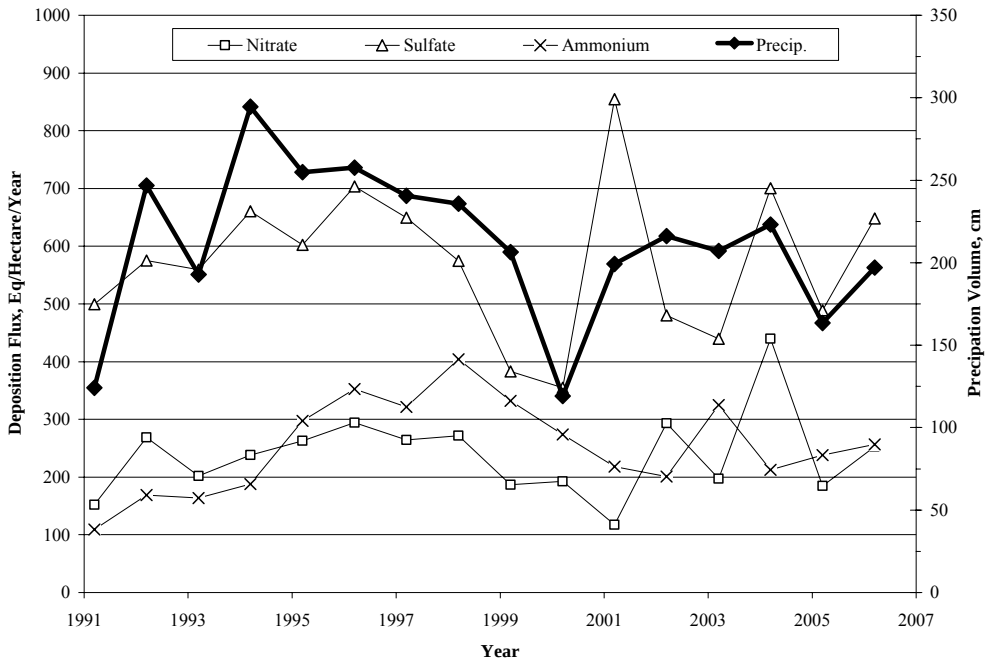

Figure 14: Depositional Flux of Nitrate, Sulfate, and Ammonium with Precipitation for OS

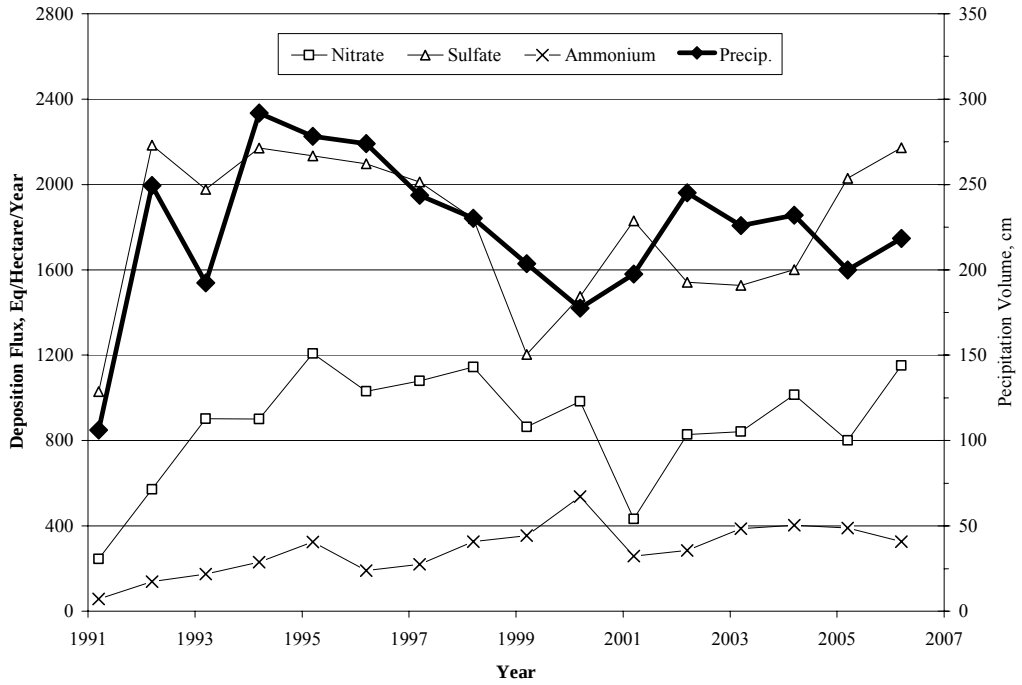

Figure 15: Depositional Flux of Nitrate, Sulfate, and Ammonium with pH for TF

would be expected.

Seasonality

Seasonality trends were presented to show the relationships of parameters to pH over a 1-year cycle. To generate the time variable of the seasonal trends, the year day was converted to radians by the following equation: θ = year day * 2 * PI / 365. A linear regression was run for each parameter with the following model: Trend = *A* Sin(θ) + *B* Cos(θ) + Constant. The absyssa in each figure is day of the year, therefore; 1 is January 1. Spring started at about day 81 and ended at about day 170. In general, summer was from day 171 to day 260; autumn was from day 261 to day 350; and winter was from day 351 to day 80. Figures 16, 17, and 18 showed the seasonal relationships of some of the key water quality parameters for SW, OS, and TF respectively.

Figure 16 showed the seasonality for chloride, nitrate, sulfate, and pH for SW. As the pH trend increased in the spring, nitrate and sulfate trends increased. Chloride trend reached an annual low in early spring and increased through the season. In summer pH increased while nitrate and chloride decreased; sulfate remained relatively constant. In early summer pH reached the annual peak and nitrate and sulfate reached annual lows. As autumn progressed pH decreased while nitrate and sulfate increased. Laudon and Bishop (2002) found that in autumn especially following an arid summer stream pH values would drop between 1.0 and 2.4 pH units. The same pattern was seen in this study where the pH drop from year day 200 to year day 10 was 0.3 pH units. Chloride reached the annual peak in early autumn. In winter, pH reached the annual low while sulfate and nitrate had relative peaks and then decreased; chloride decreased.

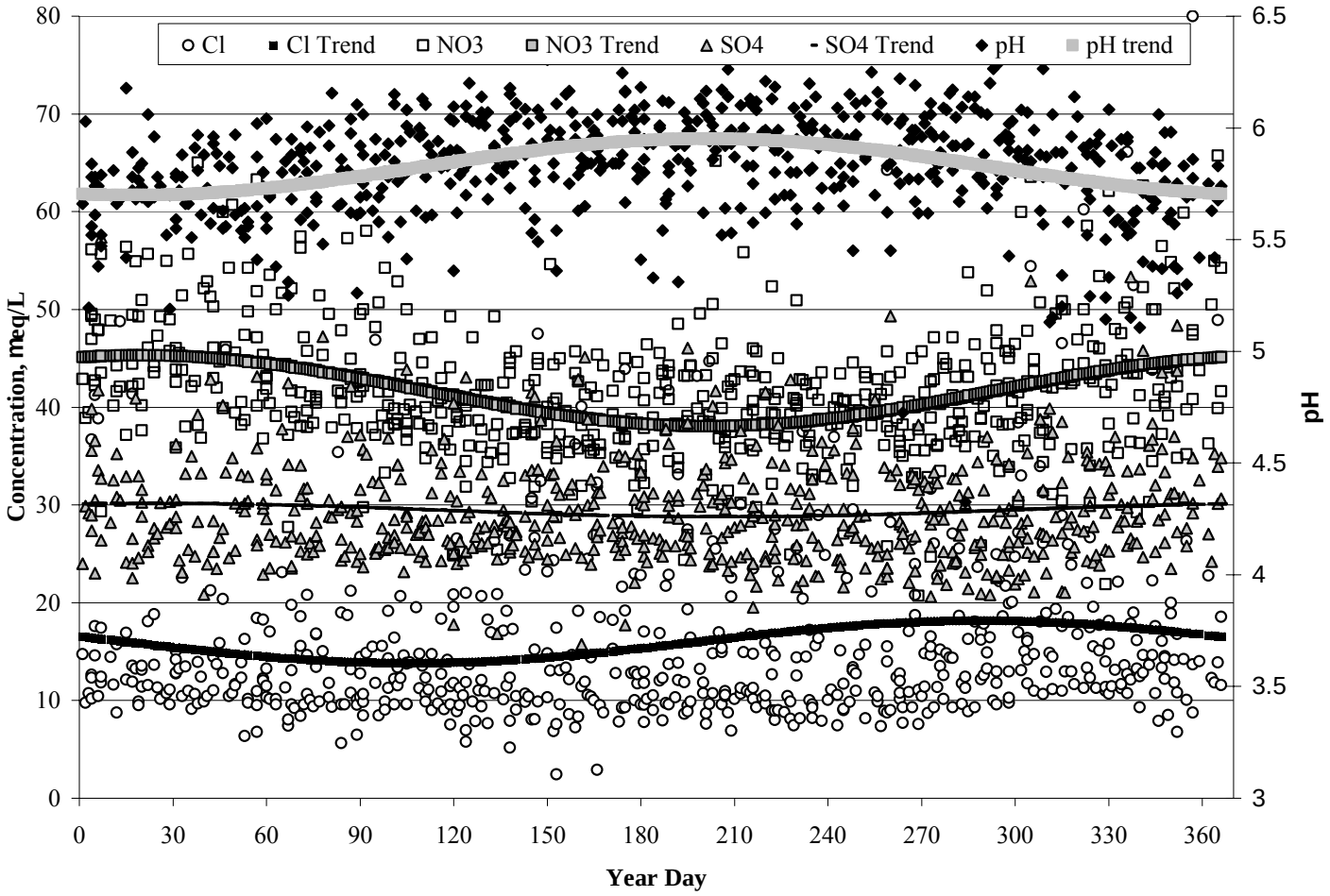

Figure 16: Seasonality Chloride, Nitrate, Sulfate, and pH for SW

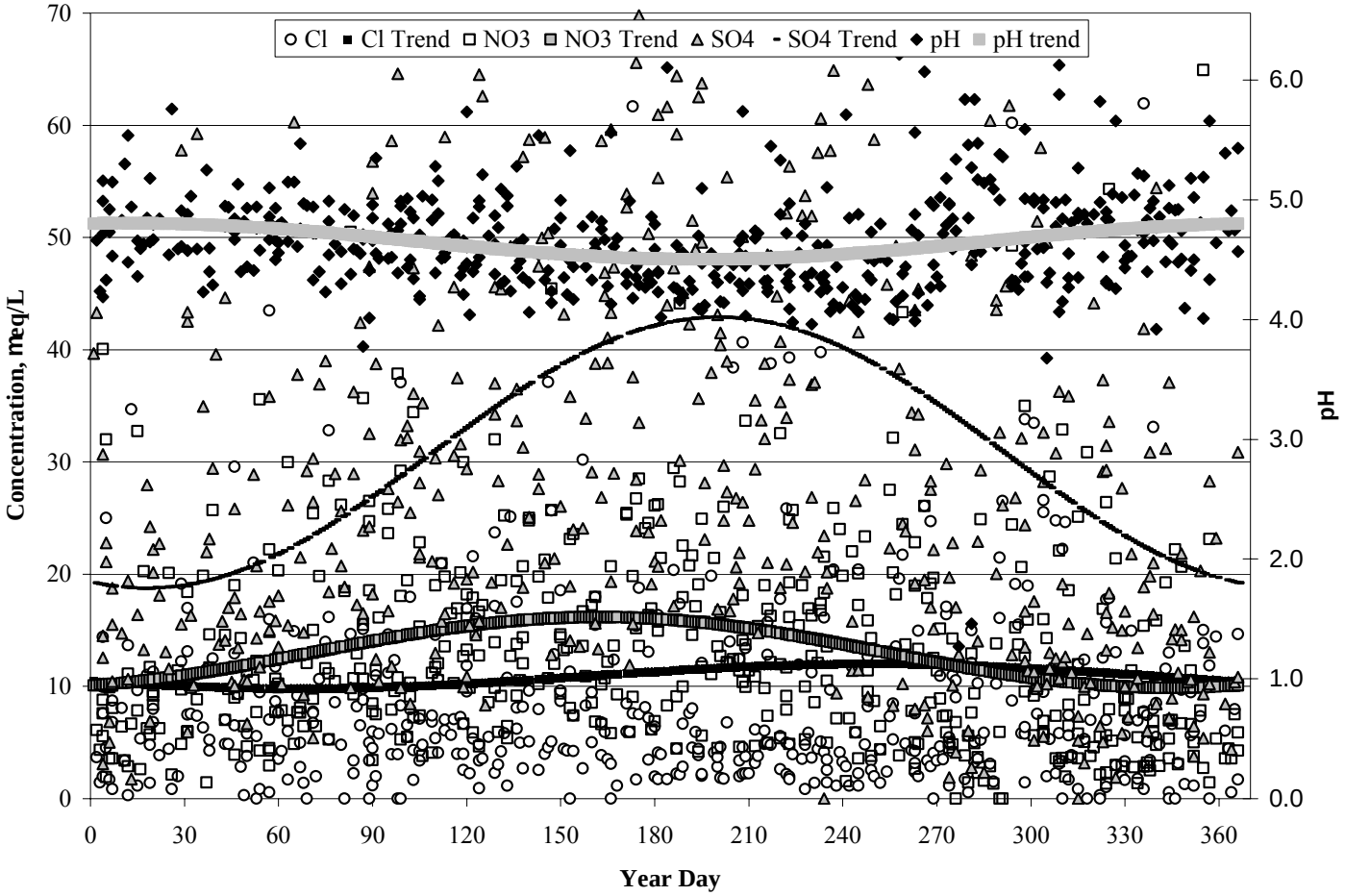

Figure 17: Seasonality Chloride, Nitrate, Sulfate, and pH for OS

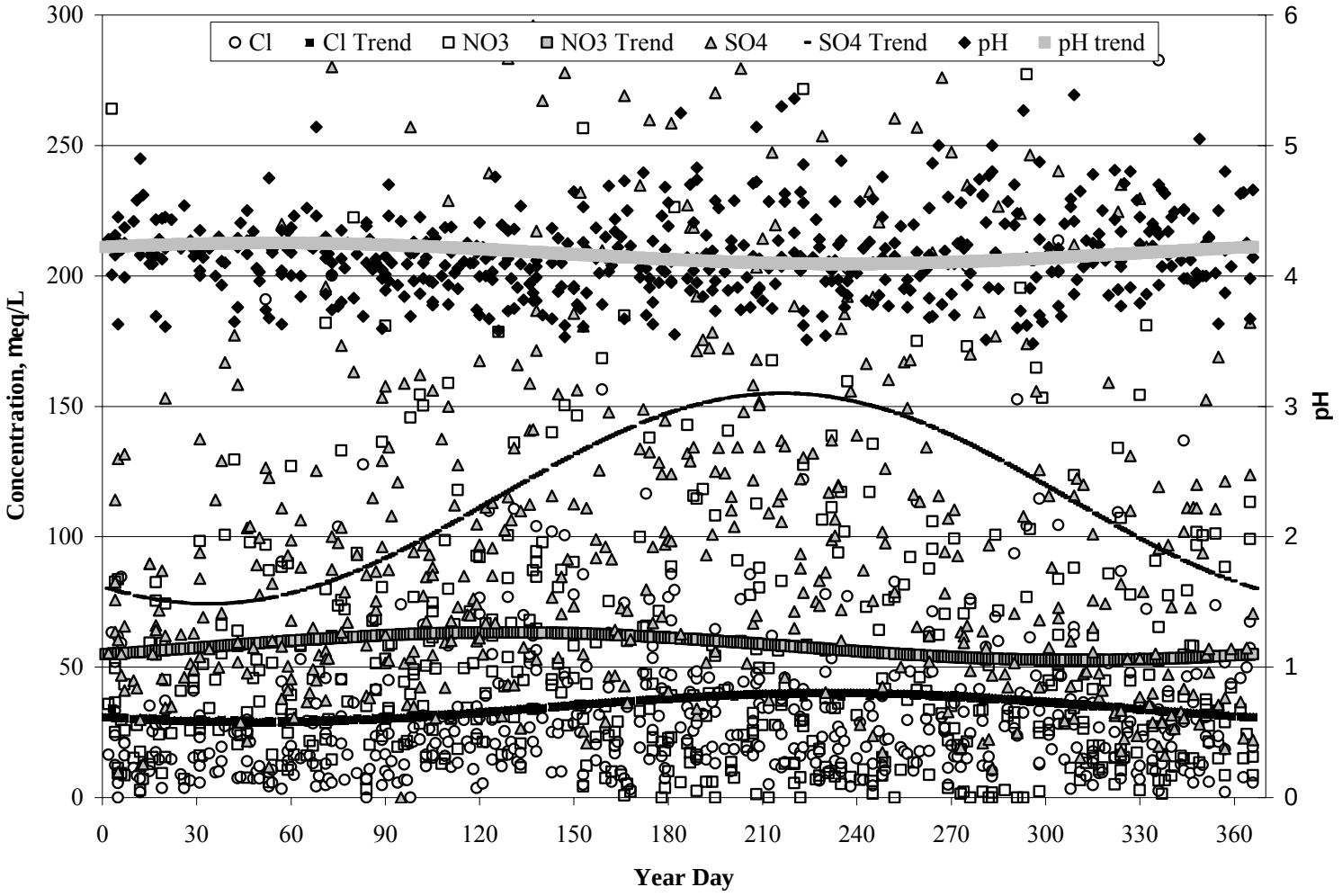

Figure 18: Seasonality Chloride, Nitrate, Sulfate, and pH for TF

Nitrate and sulfate followed a similar trend in stream water having peaks in late autumn/early winter and lows in late spring/early summer. When pH values were lowest, nitrate and sulfate values were highest and vice versa. This is consistent with the assumption that nitrate and sulfate are the primary sources of acid in the stream water (Driscoll, 2002). Nitrate concentrations at SW were about 10 to 15 μeq/L higher than sulfate concentrations. Sulfate trend for SW was relative constant having a net difference from low to peak of about 2 μeq/L. Chloride followed a similar pattern to nitrate and sulfate patterns except in autumn when chloride concentrations remained relatively constant.

Annual trends in precipitation water quality parameters were plotted in Figure 17. pH at OS exhibited the opposite seasonal pattern as SW with low occurring in the summer and peak occurring in the winter. Sulfate had an opposite pattern to the SW with concentrations increased about 125% from 19μeq/L in winter to 43μeq/L in summer. This larger amount of sulfate deposition may coincide with the large influx of motor vehicle into the GRSM to see the autumn leaves (GRSM) and with higher electricity demand resulting from hot temperatures. Sulfate trend was higher than nitrate trend by as much as 30μeq/L. Nitrate concentrations in precipitation did not mimic that of stream water. Nitrate concentrations at OS appear to have been relatively constant throughout the year except in spring when there was an increase. OS chloride trend followed the same pattern as that of SW stream.

Trends in TF water quality parameters were plotted in Figure 18. pH remained relatively constant through out the year except in the summer when there was a decrease. TF sulfate, like OS sulfate, showed peak in summer. pH trend had a low corresponding

to sulfate peak. Like OS, TF sulfate concentrations were higher than nitrate. Nitrate concentrations were highest in spring. TF chloride followed a similar pattern to OS chloride with consistent values throughout the year except for an increase in autumn.

Flow and pH for both streams were plotted in Figure 19. Both streams had very similar results as would be expected. The trend relationship of pH to flow shows that lower pH values occurred at higher flows. Although somewhat counterintuitive, as dilution is a factor, this was consistent with several other studies (Laudon and Bishop, 2002; Wigington et al, 1996b). This indicated that decreased stream water pH was caused partly by a mechanism of precipitation flushing dry deposition into the stream, not solely from a chemical quality of the precipitation.

Statistical Analysis: Bivariate Correlations

Bivariate correlations were calculated for key SW water quality parameters and the primary variables. Primary variables were described in the Background chapter. The correlations defined the relationships of stream water responses to inputs into the system. Table 5 showed only the significant correlations in order of strongest to weakest.

Time variables (date, dry_days, and dry_chem) and amount of precipitation appeared to be strong drivers of the stream water quality. Date was strongest correlation to nitrate and aluminum, indicating a strong long-term trend, which was presented in Table 4. The precipitation variables had strong correlations to nitrate; Dry_Chem had the fourth strongest correlation and Dry_Days had the sixth. Also, Dry_Days had the third strongest correlation to Aluminum. Dry_Days and Dry_Chem related wet and dry deposition to water quality, therefore; that these were both strong drivers indicated that

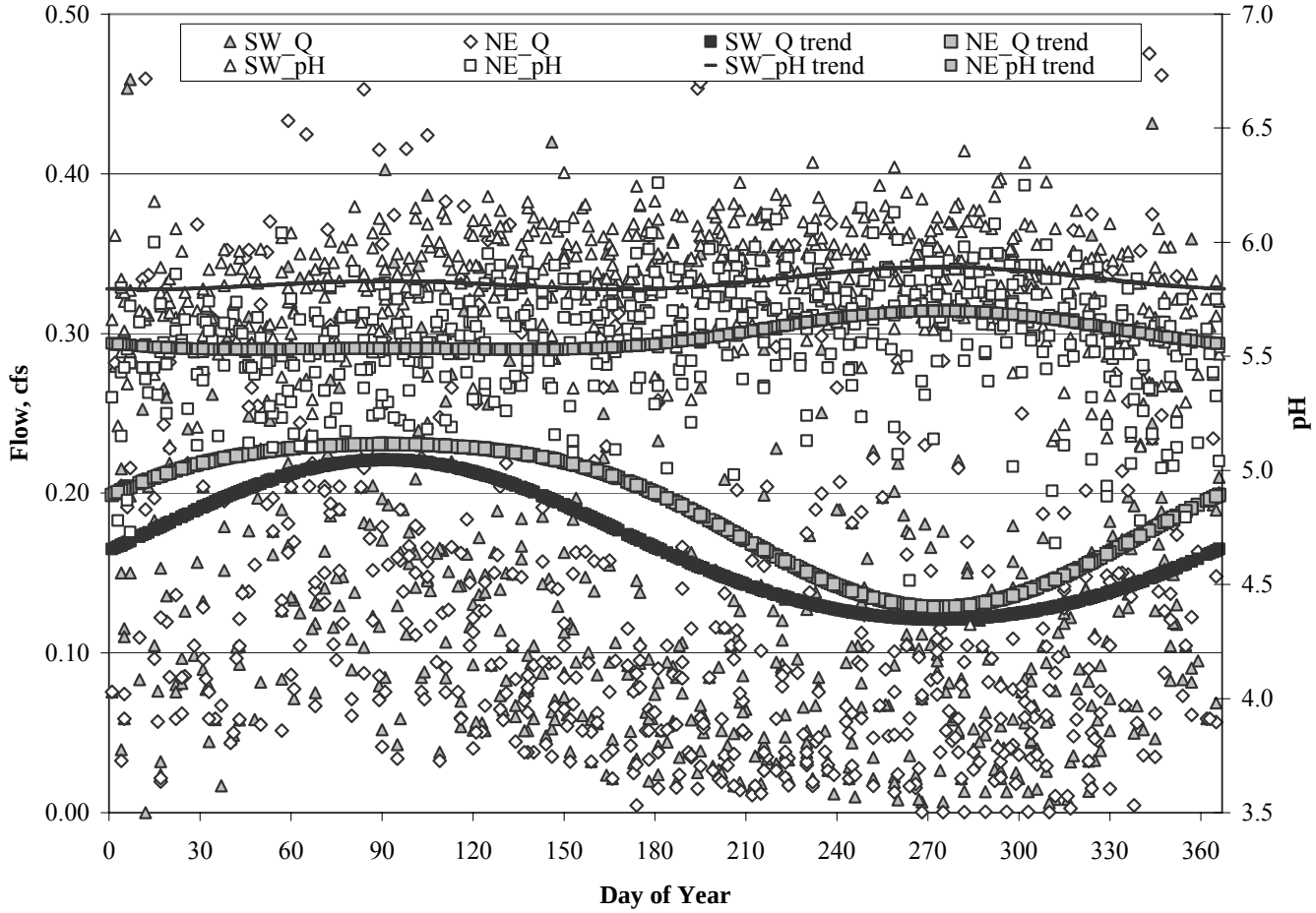

Figure 19: Seasonality Flow and pH for NE and SW

Table 5: Stream Water Quality Parameters with Primary Variables of Significant Correlation

pH		Nitrate		Sulfate		ANC		Chloride		Conductivity		Aluminum	
Variable	CC	Variable	CC	Variable	CC	Variable	CC	Variable	CC	Variable	CC	Variable	CC
TF_Vol	-.270(**)	Date	-.314(**)	SW_Q	.406(**)	SW_Q	-.289(**)	OS_Cl	.368(**)	OS_Mg	-.186(**)	Date	-.236(**)
OS_Vol	-.245(**)	OS_Mg	-.195(**)	TF_Vol	.314(**)	TF_K	.265(**)	OS_Cl_Flux	.243(**)	OS_SO4	-.165(**)	OS_H_Flux	.192(*)
SW_Q	-.234(**)	OS_Ca	-.162(**)	OS_Vol	.272(**)	TF_Vol	-.262(**)	TF_Cl	.230(**)	OS_Cond	-.154(**)	Dry_Days	-.174(*)
TF_H_Flux	-.226(**)	OS_H	-.152(**)	TF_H_Flux	.233(**)	TF_Mg	.215(**)	SW_Q	-.161(**)	OS_NO3	-.139(**)	--	--
OS_SO4	.225(**)	Dry_Chem	-.125(**)	TF_SO4_Flux	.231(**)	TF_Ca	.212(**)	Date	.158(**)	TF_NH4	-.137(**)	--	--
TF_Ca	.218(**)	OS_NH4	-.124(**)	TF_Ca	-.203(**)	OS_Vol	-.210(**)	TF_Cl	.158(**)	OS_Ca	-.136(**)	--	--
TF_Mg	.213(**)	Dry_Days	.115(**)	TF_Mg	-.195(**)	TF_SO4	.207(**)	OS_K	.154(**)	OS_N	-.133(**)	--	--
OS_Cond	.195(**)	OS_Vol	-.107(**)	TF_Cl	.183(**)	OS_SO4	.196(**)	OS_Na	.134(**)	TF_Cl	.133(**)	--	--
TF_K	.190(**)	OS_NH4_Flux	-.105(**)	OS_Cond	-.177(**)	OS_Cl_Flux	-.186(**)	TF_N	.122(**)	TF_Vol	.132(**)	--	--
TF_SO4	.181(**)	OS_N	-.103(**)	Dry_Days	-.165(**)	TF_NH4_Flux	-.178(**)	TF_K	.118(**)	OS_pH	.124(**)	--	--
OS_Cl_Flux	-.176(**)	OS_SO4_Flux	-.099(**)	OS_NO3	-.164(**)	TF_NO3_Flux	-.167(**)	TF_NO3	.108(**)	TF_Ca	-.118(**)	--	--
TF_Cl	-.176(**)	TF_Vol	-.094(**)	TF_N	-.163(**)	TF_Cond	.158(**)	TF_Na	.105(**)	TF_NO3_Flux	.116(**)	--	--
TF_Cond	.175(**)	TF_K	-.087(**)	OS_SO4_Flux	.153(**)	TF_H_Flux	-.147(**)	Year_Day	.103(**)	TF_Mg	-.115(**)	--	--
OS_NO3	.173(**)	TF_NO3	.083(**)	OS_NO3_Flux	.149(**)	OS_Cond	.147(**)	TF_NH4	.100(**)	TF_H_Flux	.113(**)	--	--
OS_N	.160(**)	TF_H	.081(**)	TF_Cond	-.141(**)	TF_Cl	-.146(**)	OS_SO4_Flux	-.099(**)	TF_SO4	-.105(**)	--	--
TF_NH4_Flux	-.152(**)	Year_Day	-.080(**)	TF_NO3_Flux	.141(**)	OS_NO3	.139(**)	TF_SO4_Flux	-.099(**)	OS_H	-.102(**)	--	--
TF_NO3_Flux	-.144(**)	SW_Q	-.079(**)	OS_Mg	-.140(**)	OS_pH	-.133(**)	OS_Ca	.077(*)	OS_NH4	-.100(**)	--	--
OS_Mg	.139(**)	TF_pH	-.078(**)	OS_Ca	-.138(**)	Year_Day	.130(**)	TF_NH4_Flux	.075(*)	OS_Vol	.081(**)	--	--
OS_Ca	.138(**)	OS_NO3_Flux	-.074(*)	OS_H_Flux	.137(**)	TF_pH	-.128(**)	OS_SO4	-.070(*)	OS_Cl_Flux	.079(*)	--	--
OS_H_Flux	-.131(**)	TF_N	.069(*)	OS_SO4	-.136(**)	TF_H	.126(**)	TF_NO3_Flux	.065(*)	Date	-.076(**)	--	--
TF_SO4_Flux	-.121(**)	OS_Cl_Flux	-.067(*)	TF_NO3	-.133(**)	Date	-.111(**)	TF_H_Flux	-.062(*)	TF_SO4_Flux	.071(*)	--	--
OS_NH4	.121(**)	TF_Cond	.064(*)	TF_SO4	-.133(**)	OS_N	.091(**)	--	--	SW_Q	.067(*)	--	--
OS_NO3_Flux	-.099(**)	OS_SO4	-.063(*)	TF_K	-.132(**)	TF_Cl	.089(**)	--	--	TF_N	-.064(*)	--	--
TF_NO3	.094(**)	TF_Cl	-.062(*)	OS_N	-.131(**)	OS_NH4_Flux	-.088(**)	--	--	Year_Day	.056(*)	--	--
OS_pH	-.086(**)	--	--	TF_Cl	-.129(**)	TF_SO4_Flux	-.080(**)	--	--	--	--	--	--
TF_Cl	.081(**)	--	--	OS_pH	.129(**)	OS_NO3_Flux	-.080(*)	--	--	--	--	--	--
Dry_Days	.080(*)	--	--	TF_NH4	-.127(**)	OS_Cl	-.076(*)	--	--	--	--	--	--
TF_N	.079(**)	--	--	TF_pH	.113(**)	OS_Na	-.067(*)	--	--	--	--	--	--
TF_H	.072(*)	--	--	OS_NH4_Flux	.108(**)	Dry_Chem	-.062(*)	--	--	--	--	--	--
TF_pH	-.068(*)	--	--	OS_Cl_Flux	.103(**)	--	--	--	--	--	--	--	--
Dry_Chem	-.067(*)	--	--	TF_H	-.099(**)	--	--	--	--	--	--	--	--
Year_Day	.058(*)	--	--	OS_Cl	-.097(**)	--	--	--	--	--	--	--	--
Date	-.056(*)	--	--	OS_NH4	-.092(**)	--	--	--	--	--	--	--	--
--	--	--	--	OS_K	-.091(**)	--	--	--	--	--	--	--	--
--	--	--	--	Dry_Chem	.087(**)	--	--	--	--	--	--	--	--
--	--	--	--	TF_NH4_Flux	.076(*)	--	--	--	--	--	--	--	--

(**) Correlation is significant at the 0.01 level (2-tailed)

(*) Correlation is significant at the 0.05 level (2-tailed)

nitrate concentration in stream water was a function of both the mechanism and the chemistry of precipitation as explained above.

Amount of precipitation was represented by SW_Q, OS_Vol, and TF_Vol. Stream flow, designated as SW_Q, was the strongest correlation for sulfate and ANC. It was third for pH and fourth for chloride. The three strongest correlations to pH were all amount of precipitation variables: TF_Vol, OS_Vol, and SW_Q respectively, and not OS_pH or TF_pH. This was consistent with other research, and indicated that stream water pH may result from the mechanism of precipitation and not the chemistry of the precipitation itself (Roby, 2005 and Cook, 1992). Like pH, sulfate had the precipitation volume variables for the first three strongest correlations. Cook and others explained that this correlation may occur because during storms sulfate from dry deposition in the upper layers of soil is flushed through by the precipitation. ANC gave similar results with two of the precipitation volume variables in the first three and the other precipitation variable as the sixth strongest correlation. Again, this indicated that dry deposition and the mechanism of precipitation had a key relationship for many water quality parameters.

Chloride and conductivity were not necessarily indicators of water quality and clearly were driven more by deposition, especially OS. The three strongest correlations to chloride were OS_CL, OS_Cl_Flux, and TF_Cl. This clearly indicated that chloride deposition was a main driver of this parameter. Precipitation and date also had influence as SW_Q and date were the fourth and fifth strongest correlation to chloride. OS variables were the top four strongest correlations to conductivity. Conductivities for OS and SW were more strongly correlated than TF and SW most likely because of dry deposition at TF allowed conductivity to accumulate. The dry deposition accumulation

between precipitation events most likely explains the correlation of stream water pH to the precipitation. In other words, the more it rained; the more acid was washed into the stream.

Statistical Analysis: Stepwise Multilinear Regression

Table 6 showed the regressions models for SW key water quality parameters including: ANC, pH, conductivity, chloride, nitrate, and sulfate. The adjusted R-square values and p-values were included in the table. All of the models showed significance with p-values less than 0.001. The number of entries (N) for the models ranged from 430 to 574.

The model for SW ANC showed that ANC increased with the natural log of OS sulfate; decreased with TF nitrate flux, the reciprocal of OS pH, and OS chloride. The adjusted R-square is 0.257. OS sulfate appeared in most of the models.

The model for SW pH showed that pH increased with the square root of OS sulfate; decreased with OS hydrogen flux, TF inorganic nitrogen, and OS magnesium squared; and increased with dry days (see primary variables in Methods chapter).

The model for SW conductivity showed that conductivity increased with TF nitrate flux; decreased with the square root of OS sulfate; increased with TF conductivity; decreased with TF sulfate and TF hydrogen; increased with OS hydrogen flux; decreased with OS nitrate flux; and increased with dry_chem (see primary variables in Methods chapter). The model for SW chloride showed that chloride increased with OS chloride and TF chloride; decreased with the natural log of OS sulfate; and increased with year day, OS nitrate, and OS sodium. The model for SW nitrate showed that nitrate decreased with date, year day, and OS ammonium flux. The model for SW sulfate

Table 6: Models for Key Water Quality Parameters with Adjusted R-Square, P-value, and Number of Observations

Key Water Quality Parameter	Model	Adjusted R-Square	P-Value	N
ANC	= 23.1012 + 6.1684*Ln(OS sulfate) - 3.485E-4*(TF nitrate flux) - 121.384*(1/OS pH) - 0.0865*(OS chloride)	0.257	<0.000	430
pH	= 5.5159 + 0.0916*(OS sulfate)^0.5 - 1.950E-4*(OS hydrogen flux) - 7.444 E-4*(TF inorganic nitrogen) - 1.0507E-3*(OS magnesium)² + 0.0157* (dry days)	0.443	<0.000	432
Conductivity	=12.742 + 3.630E-4*(TF nitrate flux) - 0.2365*(OS sulfate)^0.5 + 0.04718*(TF conductivity) - 0.01067*(TF sulfate) - 0.01128*(TF hydrogen) + 1.053E-3*(OS hydrogen flux) - 2.437E-3*(OS nitrate flux) + 0.0503*(dry chem)	0.316	<0.000	452
Chloride	= 22.960 + 0.0744*(OS chloride) + 0.0522*(TF chloride) - 5.709*Ln(OS sulfate) + 0.0174*(year day) + 0.3373*(OS nitrate) + 0.0516*(OS sodium)	0.248	<0.000	453
Nitrate	= 299.2169 - 1.931E-8*(Date) - 0.0166*(year day) - 6.123E-3*(OS ammonium flux)	0.328	<0.000	433
Sulfate	=31.1512 + 0.1036*(TF precipitation) - 5.2123E-4*(TF ammonium)² - 0.3863*(dry days) - 0.1105*(OS conductivity) + 1.4660E-7*(TF hydrogen flux)²	0.202	<0.000	574

showed that sulfate increased with TF precipitation; decreased with TF ammonium squared, dry days and OS conductivity; and increased with the TF hydrogen flux squared.

The model results supported other results that sulfate and nitrate deposition are the primary drivers of stream water quality (DeWalle and Swistock, 1995; Nodvin *et al.,* 1995; Brewer *et al.,* 2003; Van Miegroet *et al.,* 2001; Weathers *et al.,* 2006; etc). The primary drivers of sulfate and nitrate in the stream, however, are the time variables and amount of precipitation and not as much the deposition variables. Also, ammonium, the other contributor of acid deposition, appears in the model as a driver of stream nitrate and sulfate.

The adjusted R-square values showed that the models did not explain large portions of the variation of the data set; values ranged from 0.202 to 0.443. Modeling requires a finite number of independent variables and because natural environments have an infinite number of independent variables, it makes modeling challenging.

Conclusions

Long-term trends exist in the water chemistry for rainfall, throughfall, and streamwater at the NDW study site in the GRSM. Nitrate and sulfate concentrations in rainfall and throughfall are decreasing with time and pH is increasing with time, indicating reduced atmospheric deposition. Water quality does not share the trend, as decreasing pH and ANC indicate degradation of the streamwater quality.

Chemical drivers of streamwater have been identified and quantified. OS sulfate is the most influential driver of streamwater ANC and pH. Depositional hydrogen ion and pH are common drivers of the key water quality parameters. Nitrate and sulfate concentrations in the streamwater are more strongly driven by time and precipitation variables than deposition of nitrogen and sulfur.

The following list summarizes the individual conclusions of this study by type of analysis that was performed:

Descriptive statistics (Table 3)

- ✓ Both OS and TF had lower ANC values than SW most likely because the stream water comes in contact with the soil and other possible ANC contributors.
- ✓ The amount of precipitation collected at OS is understandably less than at TF as a function of the collection device.
- ✓ Dry acid deposition is most likely the reason TF had the lowest mean pH value of the other collection sites.
- ✓ Chloride could be considered a tracer in this system, which shows that the stream water concentration is a function of dilution from precipitation.

- ✓ Stream water nitrate appears to follow the same trend as chloride, being a function of dilution of the TF where there is no net nitrate retention.
- ✓ Since acid deposition primarily consists of sulfuric and nitric acids, it explains why the mean sulfate concentrations at the three collection sites have the same pattern as pH with the SW sulfate concentration being less than the two precipitation sites.
- ✓ It is assumed that the ammonium is reacting in the system because a relatively low portion is leaving the system.
- ✓ The mean sodium concentrations for the three collection sites follow the same pattern as chloride and nitrate with the TF being the largest and the OS being the smallest of the three. This indicates that the dry deposition is a large contributor and that the analytes are not being held in the system but rather leaving in the stream water.
- ✓ The mean TF potassium concentration is higher than OS and SW. This pattern is consistent with chloride, nitrate, and sodium. This indicates that the dry deposition is a large contributor and that the analytes are not being held in the system but rather leaving in the stream water.
- ✓ Mean calcium concentrations are more than twice that of magnesium for all three collection sites. The mean concentrations of magnesium and calcium follow the same pattern as chloride, nitrate, sodium, and potassium. This indicates that the dry deposition is a large contributor and that the analytes are not being held in the system but rather leaving in the stream water.

- ✓ The hydrogen ion concentrations were calculated during analysis from the pH readings; therefore the mean concentration values follow the same pattern as pH.
- ✓ The mean aluminum concentration for TF is larger than for OS and SW. This is consistent with the mean pH values.
- ✓ The mean concentrations of copper and iron for all three collection sites are low compared to the other analyte concentrations and are measured in parts per million.
- ✓ The mean SW silicon concentration greater than for TF and OS. This is assumed to be a function of contact with soil.
- ✓ The mean manganese and zinc concentrations are similar at each collection site.

Time (Table 4)

- ✓ The SW ANC is decreasing at a rate of 0.05μeq/L/yr.
- ✓ SW pH is decreasing with time at a rate of 0.005 pH units per year, whereas OS and TF are increasing with time, 0.011 and 0.016 pH units per year respectively.
- ✓ Conductivity is decreasing at all three collection sites. Time trends are decreased at rates of 0.052 μeq/L/ yr, 0.209 μeq/L/ yr, and 1.305μeq/L/ yr for SW, OS, and TF respectively.
- ✓ Chloride deposition is increasing at all three collection sites at rates of 0.375 μeq/L/ yr, 0.320 μeq/L/ yr, and 0.286μeq/L/ yr for TF, OS, and SW respectively. Since both OS and TF chloride concentrations are increasing at a similar rate it is assumed that dry deposition in not the vehicle.
- ✓ Nitrate is decreasing at TF and SW at rates of 0.204 μeq/L/ yr and 0.001μeq/L/ yr, respectively, while OS is relatively constant at 0.001μeq/L/ yr. This is most likely

because OS does not allow contact with plants and soil prior to collection like TF and SW.

- ✓ Sulfate is decreasing at all three sites. TF and OS are decreasing at rates of 3.041 μeq/L/ yr and 0.160 μeq/L/ yr respectively.
- ✓ Ammonium trends are increasing at TF and OS at a rate of 1.197 μeq/L/ yr and 0.460 μeq/L/ yr respectively. Ammonium contributes to acid deposition but considerably less than nitrate and sulfate.
- ✓ Aluminum trends are relatively consistent at all three collection sites. OS and SW show that aluminum deposition is decreasing at both sits at a rate of 0.002 μeq/L/ yr.

SW seasonality (Figure 16)

- ✓ As the pH trend increased in the spring, nitrate and sulfate trends increased.
- ✓ Chloride trend reached an annual low in early spring and increased through the season.
- ✓ In summer pH increased while nitrate and chloride decreased; sulfate remained relatively constant.
- ✓ In early summer pH reached the annual peak and nitrate and sulfate reached annual lows.
- ✓ As autumn progressed pH decreased while nitrate and sulfate increased.
- ✓ Chloride reached the annual peak in early autumn.
- ✓ In winter, pH reached the annual low while sulfate and nitrate had relative peaks and then decreased; chloride decreased.

- ✓ Nitrate and sulfate followed a similar trend in stream water having peaks in late autumn/early winter and lows in late spring/early summer.
- ✓ Nitrate concentrations at SW were about 10 to 15 μeq/L higher than sulfate concentrations.
- ✓ Sulfate trend for SW was relative constant having a net difference from low to peak of about 2μeq/L.
- ✓ Chloride followed a similar pattern to nitrate and sulfate patterns except in autumn when chloride concentrations remained relatively constant.

OS seasonality (Figure 17)

- ✓ pH at OS exhibited the opposite seasonal pattern as SW with low occurring in the summer and peak occurring in the winter.
- ✓ Sulfate had an opposite pattern to the SW with concentrations increased about 125% from 19μeq/L in winter to 43μeq/L in summer.
- ✓ Sulfate trend was higher than nitrate trend by as much as 30μeq/L.
- ✓ Nitrate concentrations at OS appear to have been relatively constant throughout the year except in spring when there was an increase.
- ✓ OS chloride trend followed the same pattern as that of SW stream.

TF seasonality (Figure 18)

- ✓ pH remained relatively constant through out the year except in the summer when there was a decrease.
- ✓ TF sulfate, like OS sulfate, showed peak in summer.
- ✓ pH trend had a low corresponding to sulfate peak.
- ✓ Like OS, TF sulfate concentrations were higher than nitrate.

- ✓ Nitrate concentrations were highest in spring.
- ✓ TF chloride followed a similar pattern to OS chloride with consistent values throughout the year except for an increase in autumn.

SW stream flow and pH Seasonality (Figure 19)

- ✓ The trend relationship of pH to flow shows that lower pH values occur at higher flows.
- ✓ Decreased stream water pH is caused by a mechanism of deposition and precipitation, not from an omni-present condition.

Regression models (Table6)

- ✓ The model for ANC is a function of the natural log of OS sulfate, TF nitrate flux, the reciprocal of OS pH, and OS chloride.
- ✓ The model for pH is a function of the square root of OS sulfate, OS hydrogen flux, TF inorganic nitrogen, OS magnesium, and dry days.
- ✓ The model for conductivity is a function of TF nitrate flux, OS sulfate, TF conductivity, TF sulfate, TF hydrogen, OS hydrogen flux, OS nitrate flux, and dry_chem.
- ✓ The model for chloride is a function of OS chloride, TF chloride, natural log of OS sulfate, year day, OS nitrate, and OS sodium.
- ✓ The model for nitrate is a function of date, year day, and OS ammonium flux.
- ✓ The model for sulfate is a function of TF precipitation, TF ammonium, dry days, OS conductivity, and TF hydrogen flux.

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Appendix

Appendix A: New TF versus Old TF

Throughfall samples were collected between June 9 and November 10, 2004 by the old/winter protocol and by the new/summer, protocol. Theses samples were collected in pairs and subjected to identical test conditions. Statistical analysis was conducted on the results to determine if the collection methods yield statistically equal chemical data.

Percent differences were calculated for each pair of data. Table A-1 shows percent differences and descriptive statistics of each set of percent differences per parameter. For most key parameters, the mean percent difference is less that 10%. Some parameters are representations, or partial representations, of others, such as, H ion is also represented by pH and conductivity and TIS are partially represented by dissolved metals. Anions and cations are linked to many others as well. These links should be considered when evaluating the data. pH with a 4.4% mean difference is a better description of the results than hydrogen ion concentration as it is the actual parameter that is measured. Anions and cations, which have low percent differences, are more representative of the system than the individual ions themselves. Many of the metal ions are in very low concentrations have inherently high standard deviations while the major contributors have low percent differences such as sulfate, nitrate, ammonium, potassium, sodium, chloride, and magnesium.

A paired T-test was performed on the data. The differences in the eleven pairs were taken for each parameter, rather than the percent differences, and then those sets were evaluated. Table A-2 shows descriptive statistics with the t-statistic, significance, and correlations for each parameter. pH, hydrogen ion, and manganese are the only parameters with t-statistics outside of the $\alpha=0.05$ ($2.228 > t > -2.228$) confidence interval.

Table A-1: Percent Differences in the Pairs of Data for New and Old TF Collection Protocols

Date	Volume, cm	Cond	pH	Cl meq/L	NO3-N meq/L	SO4 meq/L	NH4-N meq/L	H ion conc, meq/L	ICP Na meq/L	ICP K meq/L	ICP Mg in meq/L
06/09/04	19.94%	-14.07%	2.32%	-7.60%	39.99%	-14.73%	--	-21.70%	-19.48%	-15.02%	-35.54%
06/23/04	29.09%	-22.17%	4.11%	-50.28%	-73.31%	-19.21%	200.00%	-36.30%	-9.57%	-2.57%	-17.80%
07/07/04	16.26%	-15.61%	4.06%	-10.23%	-44.76%	-20.81%	--	-38.94%	-65.65%	-26.69%	-72.10%
07/22/04	-16.09%	-9.36%	6.54%	26.42%	114.46%	31.54%	-200.00%	-63.65%	-12.31%	-32.62%	-17.11%
08/03/04	-16.50%	2.39%	2.66%	59.43%	-38.20%	-43.54%	2.28%	-25.62%	6.56%	25.39%	80.94%
08/17/04	10.55%	-4.37%	5.15%	22.87%	39.50%	6.83%	-200.00%	-47.24%	179.87%	4.40%	16.11%
09/01/04	24.50%	-8.11%	1.87%	24.69%	153.23%	72.08%	-59.56%	-17.81%	-200.00%	-43.28%	-6.83%
09/15/04	-58.51%	-4.41%	5.74%	17.13%	-171.86%	-57.60%	21.29%	-55.38%	200.00%	49.67%	33.66%
10/27/04	27.87%	-22.99%	5.79%	-8.44%	-1.59%	-22.84%	110.68%	-55.76%	-13.94%	-6.74%	-28.42%
11/10/04	23.20%	-31.69%	9.03%	5.50%	-12.94%	-8.78%	63.38%	-84.70%	-22.61%	8.52%	17.94%
Average	6.03%	-13.04%	4.73%	7.95%	0.45%	-7.71%	-7.74%	-44.71%	4.29%	-3.89%	-2.92%
Median	18.10%	-11.71%	4.63%	11.31%	-7.26%	-16.97%	11.78%	-43.09%	-13.13%	-4.66%	-11.97%
Minimum	-58.51%	-31.69%	1.87%	-50.28%	-171.86%	-57.60%	-200.00%	-84.70%	-200.00%	-43.28%	-72.10%
Maximum	29.09%	2.39%	9.03%	59.43%	153.23%	72.08%	200.00%	-17.81%	200.00%	49.67%	80.94%
Std dev	28.14	10.35	2.19	29.47	93.26	37.23	141.32	20.87	114.43	27.85	42.30

-- Ammonium concentration less than detection limits was found in one or both of the samples for this collection.

Table A-1: Cont.

Date	IC Ca, meq/L	Al, ppm	Cu, ppm	Fe, ppm	Mn, ppm	Si, ppm	Zn, ppm	IC Anions	Cation Sum	Total Ionic Strength
06/09/04	-20.63%	-55.76%	200.00%	-13.18%	-36.96%	-89.13%	-156.25%	0.67%	-20.26%	-14.11%
06/23/04	-1.71%	2.37%	--	45.58%	-0.09%	13.92%	200.00%	-36.63%	6.69%	-25.31%
07/07/04	-2.35%	-61.51%	--	-23.31%	-17.07%	-45.14%	-56.17%	-18.78%	-28.05%	-29.82%
07/22/04	-5.88%	-19.41%	-21.93%	28.10%	-54.37%	-10.80%	-45.26%	47.03%	-20.87%	1.42%
08/03/04	38.25%	-22.72%	16.74%	0.32%	32.31%	-11.54%	-78.97%	-22.98%	22.77%	-9.39%
08/17/04	30.06%	40.49%	-74.54%	1.05%	-114.29%	8.65%	150.28%	19.00%	-25.39%	-23.12%
09/01/04	22.35%	-4.46%	78.89%	6.00%	-140.82%	-13.28%	182.57%	81.51%	-34.56%	6.40%
09/15/04	49.06%	-12.91%	51.72%	76.28%	-163.43%	-66.67%	181.97%	-74.00%	49.54%	-28.03%
10/27/04	-19.65%	-28.97%	127.63%	15.93%	-95.56%	-13.97%	161.58%	-15.40%	-6.44%	-19.17%
11/10/04	19.43%	-58.64%	41.72%	7.42%	-58.78%	-59.04%	-32.07%	-7.41%	16.98%	-23.84%
Average	10.89%	-22.15%	52.53%	14.42%	-64.91%	-28.70%	50.77%	-2.70%	-3.96%	-16.50%
Median	8.86%	-21.06%	46.72%	6.71%	-56.58%	-13.62%	59.11%	-11.40%	-13.35%	-21.15%
Minimum	-20.63%	-61.51%	-74.54%	-23.31%	-163.43%	-89.13%	-156.25%	-74.00%	-34.56%	-29.82%
Maximum	49.06%	40.49%	200.00%	76.28%	32.31%	13.92%	200.00%	81.51%	49.54%	6.40%
Std dev	24.31	31.60	85.50	29.19	63.00	34.26	135.91	43.63	27.21	12.45

-- Copper concentration less than detection limits was found in one or both of the samples for this collection.

Table A-2: T-test Results for New and Old TF Collection Protocols

	Paired Differences						Paired Samples Correlations		
Parameter Difference	Mean	Std. Deviation	Std. Error Mean	t	df	Sig. (2-tailed)	N	Correlation	Sig.
pH	0.155	0.180	0.054	2.868	10	0.017	11	0.519	0.102
Conductivity	-0.884	13.275	4.003	-0.221	10	0.830	11	0.440	0.175
Chloride	3.784	12.531	3.778	1.001	10	0.340	11	0.775	0.005
Volume	1.911	6.543	1.973	0.969	10	0.356	11	0.534	0.090
Nitrate	9.668	34.140	10.294	0.939	10	0.370	11	0.090	0.792
Sulfate	14.911	55.479	16.727	0.891	10	0.394	11	0.452	0.163
Ammonium	-5.778	25.372	7.650	-0.755	10	0.467	11	0.423	0.194
Hydrogen	-23.755	20.906	6.303	-3.769	10	0.004	11	0.787	0.004
Sodium	-0.276	10.642	3.209	-0.086	10	0.933	11	0.568	0.068
Potassium	4.676	38.853	11.715	0.399	10	0.698	11	0.457	0.157
Magnesium	2.697	14.755	4.449	0.606	10	0.558	11	0.621	0.042
Calcium	9.598	26.439	7.972	1.204	10	0.256	11	0.645	0.032
Aluminum	-0.005	0.020	0.006	-0.878	10	0.401	11	0.587	0.058
Copper	0.006	0.013	0.004	1.422	10	0.185	11	0.167	0.624
Iron	0.007	0.014	0.004	1.669	10	0.126	11	0.673	0.023
Manganese	-0.051	0.067	0.020	-2.543	10	0.029	11	0.809	0.003
Silicon	-0.007	0.057	0.017	-0.396	10	0.701	11	0.530	0.094
Zinc	0.087	0.218	0.066	1.320	10	0.216	11	-0.394	0.231
Anions	28.357	93.398	28.161	1.007	10	0.338	11	0.240	0.477
Cations	10.913	88.355	26.640	0.410	10	0.691	11	0.482	0.133
TIS	-8.242	187.607	56.566	-0.146	10	0.887	11	0.276	0.412
Percent Difference	0.017	0.219	0.066	0.255	10	0.804	11	-0.301	0.369
Abs (Percent Difference)	-0.027	0.111	0.033	-0.807	10	0.438	11	-0.022	0.948

The Mann-Whitney non-parametric test was performed. Table A-3 shows the Mann-Whitney U, the Wilcoxon W, and Z test statistics along with the significance for each parameter.

The Mann-Whitney U is used to calculate the z-statistic, which is then used to calculate a p-value. The p-values for the hypothesis that the methods yield equal results are given for each parameter. The Wilcoxon W for n=11 at α=0.05 has a critical value of 10. Since all parameter had w-statistics of greater than 10 there is no support that the results are not equal.

All three tests indicate that the collection methods yield results that have an acceptable deviation and are not considered unequal.

Table A-3: Test statistics for Mann-Whitney for New and Old TF Collection Protocols

Parameter	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig.(2-tailed)	Exact Sig.[2*(1-tailed Sig.)]
pH	31	97	-1.937	0.053	.056(a)
Conductivity	59	125	-0.098	0.922	.949(a)
Chloride	50	116	-0.689	0.491	.519(a)
Volume	57	123	-0.230	0.818	.847(a)
Nitrate	50	116	-0.689	0.491	.519(a)
Sulfate	57	123	-0.230	0.818	.847(a)
Ammonium	56	122	-0.300	0.764	.797(a)
Hydrogen	31	97	-1.937	0.053	.056(a)
Sodium	55	121	-0.362	0.718	.748(a)
Potassium	54	120	-0.427	0.670	.699(a)
Magnesium	54	120	-0.427	0.670	.699(a)
Calcium	41	107	-1.280	0.200	.217(a)
Aluminum	54	120	-0.427	0.670	.699(a)
Copper	46	112	-0.958	0.338	.365(a)
Iron	48	114	-0.821	0.412	.438(a)
Manganese	40	106	-1.346	0.178	.193(a)
Silicon	50	116	-0.689	0.491	.519(a)
Zinc	32	98	-1.871	0.061	.065(a)
Anions	53	119	-0.492	0.622	.652(a)
Cations	51	117	-0.624	0.533	.562(a)
TIS	54	120	-0.427	0.670	.699(a)
Percent Difference	54	120	-0.427	0.670	.699(a)
Abs (Percent Difference)	52	118	-0.558	0.577	.606(a)

(a) Not corrected for ties

Appendix B: NE

Descriptive Statistics NE

Descriptive statistics including the variability of the data are presented. Table B-1 shows the descriptive statistics including mean, median, standard deviation (stdev), and coefficient of variance (CV) for NE for the following parameters: ANC, pH, conductivity, chloride, nitrate, sulfate, ammonium, sodium, potassium, magnesium,

Table B-1: Mean, Median, Standard Deviation, and Coefficient of Variance for NE

Analyte	Mean	Median	Stdev	CV
ANC, meq/L	5.28	4.00	7.48	141.75
pH	5.55	5.57	0.28	5.08
Conductivity, mS/cm2	14.29	14.22	1.78	12.48
Cl, meq/L	17.30	15.28	7.45	43.09
NO3, meq/L	42.71	42.54	7.35	17.21
SO4, meq/L	39.08	38.43	7.21	18.45
NH4-N, meq/L	1.37	0.00	4.02	292.21
Na, meq/L	26.95	25.43	9.86	36.59
K, meq/L	11.30	9.77	8.20	72.52
Mg, meq/L	20.27	20.68	3.47	17.13
Ca, meq/L	51.60	50.60	7.43	14.40
H, meq/L	3.62	2.72	3.50	96.84
Al, ppm	0.06	0.04	0.05	82.89
Cu, ppm	0.01	0.00	0.01	180.52
Fe, ppm	0.01	0.00	0.02	176.15
Mn, ppm	0.01	0.01	0.01	108.11
Si, ppm	1.61	1.65	0.27	16.55
Zn, ppm	0.03	0.02	0.10	316.07

calcium, hydrogen, aluminum, copper, iron, manganese, silicon, and zinc.

Time Trends Table NE

Linear time trends are presented NE for the following parameters: ANC, pH, conductivity, chloride, nitrate, sulfate, ammonium, and aluminum. Table B-2 shows the mean, slope, R-square, and p-value for each correlation.

Seasonality

Seasonality trends are presented to show the relationships of parameters to pH over a 1-year cycle. Figure B-1 shows the seasonality for chloride, nitrate, sulfate, and pH for NE.

SW to NE Bivariate Correlations

NE and SW streamlet water chemistries are similar as seen in Table B-3. Correlations of NE variables to their corresponding SW variables are bordered. The correlations are significant for all pairs.

Table B-2: Time Trends with Mean, Slope, R-square, and P-value for NE

Description	Mean	Slope, units/yr	R-square	P-value
ANC, μeq/L	5.28	1.565	0.072	0.000
pH	5.55	-0.025	0.013	0.120
Conductivity, μS/cm²	14.29	0.25	0.07	0.000
Cl, μeq/L	17.30	-0.675	0.035	0.010
NO3, μeq/L	42.71	-0.487	0.017	0.073
SO4, μeq/L	39.08	1.033	0.081	0.000
NH4-N, μeq/L	1.37	-1.520	0.023	0.036
Al, ppm	0.06	-0.221	0.003	0.615

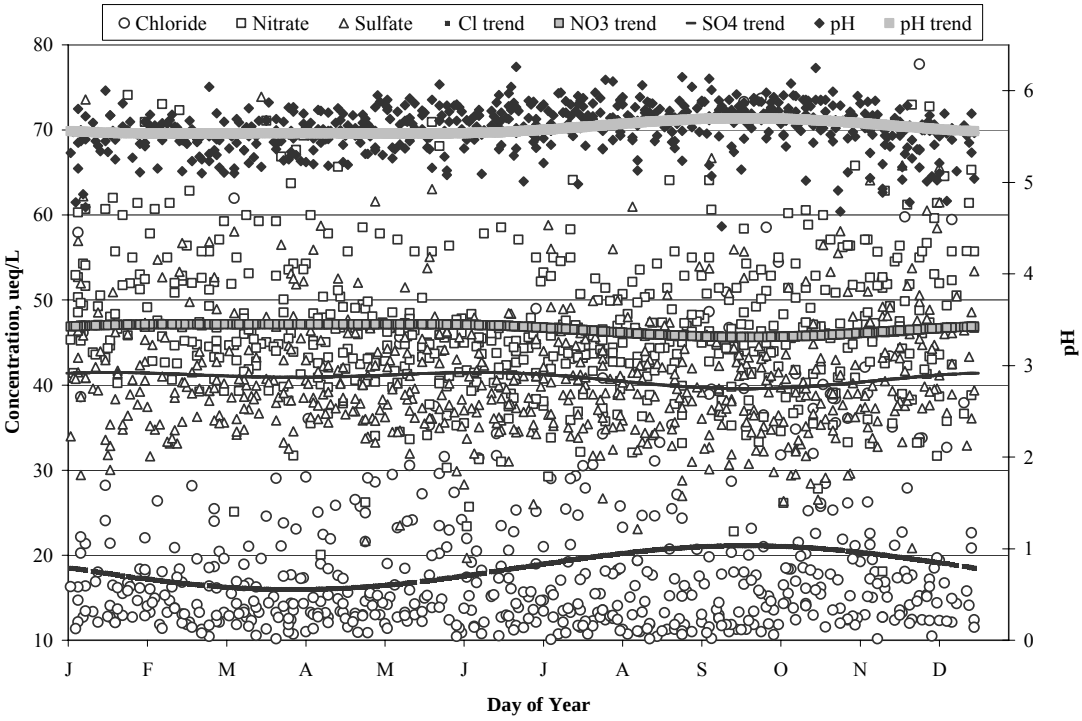

Figure B-1: Seasonality of Chloride, Nitrate, and Sulfate, with pH for NE

Table B-3: Correlations of Corresponding Variables for NE and SW

Variable	Statistic	SW_Q	SW_pH	SW_Cond	SW_ANC	SW_Cl	SW_NO3	SW_SO4	SW_Na	SW_NH4	SW_K	SW_Mg	SW_Ca
NE_Q	Correlation Coefficient	.795(**)	-.268(**)	.091(**)	-.318(**)	-.136(**)	-0.051	.388(**)	-.338(**)	-0.048	.063(*)	.076(*)	0.004
	Sig. (2-tailed)	<0.000	<0.000	0.001	<0.000	<0.000	0.068	<0.000	<0.000	0.135	0.025	0.022	0.899
	N	579	574	574	571	574	574	574	574	574	574	408	418
NE_pH	Correlation Coefficient	-.324(**)	.563(**)	-.092(**)	.338(**)	-0.041	0.026	-.200(**)	.181(**)	-0.006	-.106(**)	0.031	-.102(**)
	Sig. (2-tailed)	<0.000	<0.000	0.001	0.000	0.137	0.336	<0.000	<0.000	0.859	<0.000	0.337	0.001
	N	578	602	602	599	602	602	602	602	602	601	436	446
NE_Cond	Correlation Coefficient	.201(**)	-.165(**)	.511(**)	-.125(**)	-0.022	0.024	.237(**)	-.071(**)	0.046	.113(**)	.144(**)	.088(**)
	Sig. (2-tailed)	<0.000	<0.000	<0.000	<0.000	0.425	0.370	<0.000	0.009	0.150	<0.000	<0.000	0.005
	N	578	602	602	599	602	602	602	602	602	601	436	446
NE_ANC	Correlation Coefficient	-.340(**)	.295(**)	-0.052	.525(**)	0.022	-0.027	-.197(**)	.240(**)	0.035	-.059(*)	0.039	-0.040
	Sig. (2-tailed)	<0.000	<0.000	0.057	<0.000	0.431	0.332	<0.000	<0.000	0.264	0.031	0.225	0.205
	N	574	598	598	597	598	598	598	598	598	597	432	442
NE_Cl	Correlation Coefficient	-.180(**)	-.060(*)	0.040	-.085(**)	.548(**)	0.010	-.069(*)	.162(**)	-.072(*)	.164(**)	-.217(**)	.187(**)
	Sig. (2-tailed)	<0.000	0.027	0.139	0.002	<0.000	0.704	0.011	<0.000	0.023	<0.000	<0.000	<0.000
	N	577	601	601	598	601	601	601	601	601	600	435	445
NE_NO3	Correlation Coefficient	-0.002	-0.015	.059(*)	0.002	-.086(**)	.509(**)	-0.027	-.078(**)	0.017	0.035	.282(**)	-.225(**)
	Sig. (2-tailed)	0.956	0.576	0.030	0.936	0.002	<0.000	0.327	0.004	0.593	0.205	<0.000	<0.000
	N	577	601	601	598	601	601	601	601	601	600	435	445

Table B-3: Cont.

Variable	Statistic	SW_Q	SW_pH	SW_Cond	SW_ANC	SW_Cl	SW_NO3	SW_SO4	SW_Na	SW_NH4	SW_K	SW_Mg	SW_Ca
NE_SO4	Correlation Coefficient	.397(**)	-.176(**)	.166(**)	-.172(**)	-.074(**)	-.067(*)	.552(**)	-.200(**)	0.000	.082(**)	.078(*)	.070(*)
	Sig. (2-tailed)	<0.000	<0.000	<0.000	<0.000	0.007	0.014	<0.000	<0.000	0.989	0.003	0.015	0.028
	N	577	601	601	598	601	601	601	601	601	600	435	445
NE_Na	Correlation Coefficient	-.360(**)	.202(**)	-0.046	.131(**)	.197(**)	-0.010	-.242(**)	.485(**)	-0.020	.065(*)	-.152(**)	.122(**)
	Sig. (2-tailed)	<0.000	<0.000	0.089	<0.000	<0.000	0.727	<0.000	<0.000	0.536	0.017	<0.000	<0.000
	N	577	601	601	598	601	601	601	601	601	600	435	445
NE_NH4	Correlation Coefficient	-.099(**)	0.006	-0.032	0.011	-0.029	-0.018	-0.027	0.025	.454(**)	-0.034	-0.013	-0.014
	Sig. (2-tailed)	0.002	0.846	0.300	0.718	0.350	0.563	0.382	0.425	<0.000	0.275	0.713	0.692
	N	577	601	601	598	601	601	601	601	601	600	435	445
NE_K	Correlation Coefficient	0.054	-.143(**)	.125(**)	-.112(**)	.148(**)	0.011	.074(**)	0.022	-.073(*)	.372(**)	0.023	-0.017
	Sig. (2-tailed)	0.052	<0.000	<0.000	<0.000	<0.000	0.685	0.007	0.431	0.020	<0.000	0.471	0.587
	N	575	599	599	596	599	599	599	599	599	598	435	445
NE_Mg	Correlation Coefficient	.155(**)	0.001	.172(**)	.101(**)	-.288(**)	.232(**)	0.047	-.143(**)	.150(**)	-0.002	.755(**)	-.237(**)
	Sig. (2-tailed)	<0.000	0.967	<0.000	0.002	<0.000	<0.000	0.152	<0.000	<0.000	0.963	<0.000	<0.000
	N	387	409	409	406	409	409	409	409	409	408	389	389
NE_Ca	Correlation Coefficient	.095(**)	-.065(*)	.093(**)	-.172(**)	.188(**)	-.205(**)	.157(**)	.110(**)	-0.028	0.026	-.259(**)	.638(**)
	Sig. (2-tailed)	0.005	0.049	0.005	<0.000	<0.000	<0.000	<0.000	0.001	0.455	0.423	<0.000	<0.000
	N	399	420	420	417	420	420	420	420	420	419	390	400

Vita

Angela Vanessa (Brawley) Smith is a Sevier County, Tennessee native. Both of her engineering degrees, Civil Bachelors and Environmental Masters, were earned at the University of Tennessee, Knoxville. Angela's concentration for her masters degree was water quality. She is currently employed at Vision Engineering and Development Services, Inc. in Sevierville, Tennessee where she focuses on utilities and is preparing to earn her PE in hydraulics. Angela can be reached at abrawle1@yahoo.com.